THESIS

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SOME MEASUREMENTS OF FIBRE DENSITY

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ABSTRACT

The present investigation deals with methods of measuring fibre density and the effect of temperature and humidity.

The density values of some dry fibres have been obtained by mass per unit volume, specific gravity bottle, flotation, gradient column and Beckman methods. Pretreatment to remove any entrapped air from the fibre material included either a modified drying technique or boiling in xylene. Density determinations of dry fibres have been carried out in different organic media.

The density gradient column method was the principal method used, and it has been discussed in terms of its range, sensitivity, stability and calibration. This method was found to be more rapid and reliable than other methods for determining the density of a number of fibres.

The density values of Acrilan, cellulose acetate, nylon, polypropylene, polyethylene, polyurethane, rubber, silk, viscose rayon, Terylene, Tricel and wool fibres have been obtained in the dry state at a constant temperature 20°C. The density values for the different dry fibres reflect the major differences in fibre structure and the slight

differences that exist between modified fibres of basically similar structure.

The density of Acrilan, cellulose acetate, nylon, silk, viscose rayon, Terylene, Tricel, and wool has been investigated at a constant temperature (20°C) over a humidity range of 0% r.h. to 98% r.h. The densities of a number of these materials have also been studied at 0% and 66% r.h. over a temperature range of 20°C to 70°C. The percentage change in the density values with temperature and humidity has been calculated based on the density of dry fibres at 20°C.

The effect of moisture adsorption on the density of hydrophilic fibres has been to increase density at low humidities with the absorption of small amounts of water, followed by a fall in density as more water is absorbed. The effect of temperature on the density of fibres has been a decrease in density with an increase in temperature.

These phenomena have been considered in relation to the structure of the fibre. As would be expected hydrophobic fibres such as polyethylene and polypropylene were found to be affected by changes in temperature only, but the order of change due to temperature and humidity of the hydrophilic

fibres varied considerably. Terylene and nylon were least affected by humidity as their regain values would lead one to expect and because there are fewer active groups and side groups in the molecules of these fibres. Changes with temperature reflected the relative coefficients of cubical expansion of these materials. In Acrilan the effect of regain and temperature was slightly more predominant probably due to the fact that there may be comparatively strong attractive forces between neighbouring molecules and because of the polar nature of the -CN groups. Wool, silk and viscose rayon also showed a more predominant effect than nylon and Terylene. This may be due to the fact that in cellulose there are hydroxyl groups to which water molecules can be attached by hydrogen bonds, while in proteins there are carbonyl groups in the main chain, and other active groups in the side chains.

Cellulose acetate, and Tricel showed less marked effect with regain and temperature compared with wool, silk and viscose rayon. This may be due to the fact that there are fewer active groups in the molecules of the fibres, as in cellulose acetate the hydroxyl groups are replaced by acetyl

groups and Tricel besides being more highly crystalline than cellulose acetate absorbs less water because of the removal of all hydrophilic hydroxyl groups.

Finally differences in the density of types of polypropylene, polyurethane and viscose rayon have been found and ascribed to differences thought to exist in their respective physical structures.

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CHAPTER 1 : INTRODUCTION AND LITERATURE SURVEY

1. DEFINITIONS

The density of a material may be defined as the mass contained in unit volume of the material and is usually expressed in grammes per cubic centimetre. The relative density or specific gravity of a material is the ratio of the weight of the material at a particular temperature to the weight of an equal volume of water at the same temperature.

In the case of porous substances such as textile fibres in which air is occluded in the pores, a distinction may be drawn between the apparent and true density[1]. The apparent density of a fibre is obtained if the volume measured is the apparent volume of the fibre, including pores and spaces, while the true density of a fibre is obtained if the volume measured is that occupied by fibrous material only. Another term used with textile fibres is linear density which is defined as the mass per unit length of a fibre and is usually expressed in millitex (milligrammes per kilometre).

Finally the specific volume of a material is the reciprocal of the density, the volume per unit mass being expressed as cubic centimetres per gramme.

2. METHODS OF MEASUREMENT

Mass per unit volume

This is the most direct method for determining the density of a solid provided that the weight and volume of the material may be measured accurately. Coates[2] considered that it was possible to calculate the volume of glass fibres from measurements of their dimensions, but that problems of accurate measurement, and the number of measurements required made the method laborious. No other textile reference has been found, which would suggest that this method is not so attractive as its apparent initial simplicity would suggest.

Specific Gravity Bottle and Pycnometer.

The density of a liquid may be determined using a specific gravity bottle or pycnometer, but the method may be extended to solids provided they are heavier than the immersion media and are insoluble in it. King[3] measured the density of different wool fibres in water, and in organic liquids, using a specific gravity bottle and showed that organic liquids were not appreciably absorbed when wool was exposed to their vapour, and that there was no observable swelling of the fibre in the water free liquid. He showed further that the values of density

for the dry fibre obtained using benzene, nitrobenzene, toluene, and carbon tetrachloride as the immersion media were practically identical, and that no penetration had occurred with any of the liquids, a conclusion later substantiated by Speakman[4], in his studies of the structure of the wool fibres. King concluded that the density as measured by displacement of these organic liquids, was the true density of wool, while that measured in water (a higher value) was regarded as an apparent density.

Davidson[5] measured the density of cellulose in water, helium and in some organic liquids. The values found in organic liquids, such as toluene and heptane, were slightly lower than the densities found in helium, whilst the density in water was much higher than in either of the non-swelling fluids. According to Davidson, the density in helium is the true density, as helium gas is not compressed and it was assumed that the small helium atoms could fill up all the pores, whereas although water also penetrates the pores, it is compressed under the influence of strong molecular forces, leading to an underestimation of volume, and hence a high value of density.

Weltzien[6] reported that it might be possible that certain capillary spaces in the fibre inaccessible to helium, could be occupied by water, in

which case the density measured in helium must be considered too low. Filby and Maass[7] determined the density of cotton in benzene and reported it as the true density, while Lauer and Westerman[8] who measured the density of cellulose in water and in methyl alcohol and ethyl alcohol, suggested that the density in water was the true density.

Heertjes[9] determined the(true)density of mercerised Egyptian cotton in helium and found values in agreement with the values found by Davidson for mercerised Sea Island cotton, He also concluded that the apparent considerable compression of the water could not be real and that some water must in some way penetrate into the walls of the pores. From a comparison of the density figures in helium, and in water, Heertjes calculated that three percent of water penetrated completely into the crystalline part without giving rise to a dilation of the lattice, or a corresponding larger quantity penetrated partly into the surface of the micelles. He also discussed the possibility of water bound in micelles which were not crystalline, his concept of micelles being apparently not confined to the crystalline substance, but including all homogeneous solid material composing the fibre.

Stamm and Hansen[10] determined the density of cellulose in water, helium, and in organic liquids and found the density in helium to be nearer to that in water than the densities found in polar liquids which, as they cause a swelling of the material, are larger than those in non-swelling liquids. Hermans[11] rejected the density in helium as the true density because of the high density which would have to be attributed to the absorbed water. The fact that helium diffuses[12] slowly through the dry cellulose membrane suggests that it is to some extent soluble in cellulose and could be expected to give too high a value.

Wakeham[13] who measured the density of different kinds of cotton in benzene, dioctyl phthalate, and mercury, found that if fibres were cut by grinding in a ball mill and passed through a 20 mesh screen, the density of the cut fibres was always greater than that of the whole fibres. On the average, an increase in density of 0.021 g/cm^3 was obtained for cut cotton fibres measured in benzene and in dioctyl phthalate.

Blod and Frolich[14] determined the density of different cellulosic fibres in carbon tetrachloride, and their swelling in water, in order to establish the density swelling relationship. They found that as

the density of dry fibres increased, the amount of swelling decreased. The swelling in water was calculated as the weight of water retained as a percentage of the dry weight of the fibre.

Abbott and Goodings[15] determined the density of undrawn and drawn nylon in water and in benzene, and stated that the volume measured in non penetrating media such as benzene was higher than that measured in water, hence density figures were found correspondingly lower in benzene than in water. The density of natural fibres in organic liquids was investigated by Campbell and Russell.[16] They postulated that natural fibres contain pockets or pores accessible only to those liquids which can penetrate below the surface and fill these cavities. Illingworth[17] in summarizing the work which had been done on the density of cotton, regenerated cellulose, wool and silk, concluded that the liquids which penetrated the fibres did so by dissociating inter-molecular bonds between the fibre molecules, with resultant swelling of the fibre, hence the values obtained were not the true density of the material. He suggested that the values obtained by gaseous displacement with helium were nearly the true ones.

Fortes[18] determined the density of cellulose acetate yarn in various members of the homologous series of aromatic and aliphatic alcohols, aldehydes, ketones, ethers, esters, halogens, nitriles, nitrocompounds and hydrocarbons. The apparent density was found to be a function of polar groups of the molecules of the liquid medium, as well as their size and shape values at 20°C, ranging from 1.306 with carbon tetrachloride to 1.415 with n-heptaldehyde. He suggested a hydrogen bonding mechanism to explain the manner by which the liquid medium molecules penetrated the materials and commented that different rates of penetration could be expected with different denier and number of filaments.

Hydrostatic Balance

The density of both liquid and solid may be obtained by the use of a hydrostatic balance, the Principle of Archimedes stating that a body immersed in a liquid expresses a loss in weight which is exactly equal to the weight of liquid displaced. Gaines and Rutkowski[19] devised a method for measuring the densities of liquids based on this principle and found that the measurements of a number of samples

could be made very quickly, sensitivity, precision and calibration being also discussed.

Hermans et al[20] determined the density of cellulose in water, and they stated that the density in water proved to be dependent upon the preliminary treatment and upon the time which elapsed since immersion. They obtained constant and reproducible figures, after briefly boiling in water, after an interval of fifteen hours. They also stated that the figures obtained were still to some extent affected by temperature even after a correction had been made for the temperature of the water.

Flotation and Gradient Column

An obvious method of measuring the density of a solid is to observe whether the solid sinks or floats in liquids of known density. The density of the liquids can be adjusted until the material neither sinks nor floats, the density of the liquid being then taken as the density of the solid. The method has been extended to provide a column of liquid, whose density varies in a constant manner from the top to the bottom, in which the solid is allowed to find its own level of corresponding density.

Flotation method

The flotation method, using carbon tetrachloride, was first applied to fibres by Moll[21] who determined the density of cellulose fibres. Hermans[22] also worked with cellulose fibres and suspended small pellets of the fibres in carbon tetrachloride, and then varied the temperature until the fibres remained suspended in the liquid. The densities of the fibre and liquid were then the same, and knowing the values of the densities of the liquid at different temperatures the fibre density at a particular temperature could be obtained. These figures could be corrected to a standard temperature by the application of the coefficient of expansion of the liquid. The method was claimed to give the density values accurate to the third decimal place.

Sharkov and Levanova[23] determined the density of various cellulosic fibres in carbon tetrachloride. They found greater variations in density values of acetate rayon, and assumed that the properties of cellulose acetate, were affected by the composition of the medium used. They further reported that the lower the dielectric constant of the medium and the lower the swelling of the cellulose in it, the lower will be the density and the higher will be reactivity

of the cellulose to ethanolysis and hydrolysis.

Abbott and Goodings[15] modified and speeded up this method. They placed nylon fibres, chopped up to 1 mm lengths, into a tube containing a mixture of liquids of approximately the correct density. The tube was then centrifuged and if their densities were the same the fibres remained in a uniform cloud in the liquid, if they were different they accumulated into a single group, which sank or floated depending on whether the liquid density was too high or too low. By the process of trial and error, the correct density could be found. They also concluded that the density values were accurate to the third decimal place.

Craig et al[24] determined the density of acrylic fibres in liquid mixtures of carbon tetrachloride and toluene, and also by immersing the fibre sample in mercury in order to find correlation between these two methods. They found that the density in a wetting liquid decreased with increasing amounts of residual solvent left in the sample during spinning indicating the creation of non-communicating voids in the fibre. They reported that the large differences in the two densities could be partially accounted for by marked increase in the degree of crenulation of the fibre surface causing the density in mercury to be large.

Takahashi and Nukushina[25] measured the density of acrylic fibres in organic liquids in order to check the correlation with x-ray diffraction. They found no correlation with the crystallinity as measured by the x-ray diffraction method, and considered that the density seemed to be associated with the existence of microvoids. The density values were observed to be higher in organic liquids than those expected from the values of scattering power. They stated that because of heat treatment of water swollen filaments under wet conditions, the volume fraction of microvoids became very large and the size of distributions of microvoids reached an unusually large dimension, so that many voids of large size were filled up by the liquid used for the measurement of density and hence higher densities were obtained.

The use of the flotation method for determining the density of single fibres, or small bundles of fibres has been reviewed by Rochas.[26]

Density Gradient Column

None of the methods so far discussed seem to offer both the high degree of precision and the rapidity required for the measurement of a large number

of samples. The density gradient column would appear suitable in these respects.[27-33] The use of the density gradient column was first described by Linderstrom-Lang and co-workers.[34-36] A gradient was made in a vertical glass tube, and the density of microscopic droplets was determined, it being shown that a fairly stable linear density gradient could be established and maintained by the partial mixing of two organic liquids.

Boyer et al[37] who measured the rate of crystallisation of polyvinylidene chloride samples and other polymers, prepared a gradient in a measuring cylinder by taking a liquid of density greater than that required to be measured and then filling the remainder of the cylinder with a liquid of density lower than that required to be measured, bulk mixing of the two liquids being avoided. They found that it was a rapid method for the identification of the density of single polymer particle.

An alternative technique is to introduce the two liquids into the column simultaneously in such a varying proportion throughout the filling that a linear density gradient is produced immediately. Methods of doing this have been described by Anderson[38] and Tung and Taylor[39] who discussed the linear stability

of the density gradient formed by diffusion.

Tessler et al[40] who examined the influences of spinning variables on synthetic and cellulosic fibres, concluded that the gradient column was a simple and rapid method whereby the textural homogeneity of fibres could be studied. Wetlaufer[41] described a simple device for filling a density gradient column which was used by Preston and Nimkar,[42] for measuring the density of natural and synthetic fibres, the method again depending on setting up a vertical diffusion gradient between two organic liquids whose densities were above and below the density to be measured. Fibre density values found by this method agreed with those previously published in literature, and differed from one another by less than the experimental error in the examination.

Stock and Scofield[43] determined the density of wool and resin treated wool fibres, and noted that the density of wool increased uniformly up to 20 hours from 1.316 g/ cm^3, after 24 hours to a final figure of 1.319 g/cm^3, and wool containing 3.9% resin rose from 1.320 g/cm^3, and was still rising 40 hours later, when the density was 1.329 g/cm^3. They also discussed range, stability, sensitivity, and calibration.

The density of various fibres in mixtures of organic liquids was measured by Mikhailov et al[44] in order to investigate the molecular structure of the fibres. They found that the relation between the true density and the water content could be used in determining structure homogeneity of the fibres. They have further reported that improved physico-mechanical characteristics of cord fibres were brought about by uniform distribution of the inter molecular bonds ~~with respect to number of energies~~.

The density of polymeric materials in liquid mixtures of heptane and carbon tetrachloride have been obtained by Stefani et al,[45] Kennedy and Fontana,[46] Koyano and Nago,[47] and Rosenbaum.[48] They found that these liquids did not interact with the polymer, and a reliable measure of density could be obtained. Hurley and Tzentis[49] determined the density of polyacrylonitrile in a solution of heptane and carbon tetrachloride. They found the maximum densities of acrylonitrile homopolymers and copolymers containing at least 85% acrylonitrile by weight were slightly less than 1.200 g/cm^3, while the density of wet spun unstretched gel fibres which had never been dried or heated above 50°C was found to be 1.235 g/cm^3. They

reported that essentially all space within the gel fibres was accessible to the surrounding liquids, and that the density of 1.295 g/cm^3 was not caused by interaction of carbon tetrachloride with the polymer gel and they considered it a true density of polyacrylonitrile.

On the other hand Ripa and Schneider[50] measured the apparent densities of acrylic fibre, acrylic homo-polymer, co-polymer, and tripolymer gels, in different liquids and liquid mixtures.. They found that the gel densities greatly depended on the media used in the test method, because for the same gel values they obtained the values ranging from 1.12 to 1.26 in various media.. They stated that liquid polymer interaction, and preferential adsorption in binary solutions, usually took place. They further reported that the apparent densities depended on other factors such as weight, dimensions of the adsorbed molecules, and also on the surface area of polymer available for interaction.

Finally some criticism of the gradient method came from Austin and Roberts[51] who, in determining the densities of a series of laundered cotton, used both methods and considered that the gradient method of

diffusion was less reliable than the flotation method because of the greater variability of their results using the former method.

Reference values of the densities of various fibres have been shown in Table 1. together with the methods and media used.

TABLE 1

Density of fibres, comparison of values, methods, and media

Key:- Media	Method
1. Benzene	A Specific gravity Bottle
2. Carbon tetrachloride	B Pyknometer
3. Dioctylphthalate	C Hydrostatic Balance
4. Ethyl alcohol	D Flotation
5. Heptane	E Density gradient column
6. Methyl alcohol	
7. Nitrobenzene	
8. Kerosene	
9. Toluene	
10. Water	
11. Xylene	
12. Mixture of 1 and 2	
13. Mixture of 1 and 7	
14. Mixture of 4 and 10	
15. Mixture of 5 and 2	
16. Mixture of 8 and 10	
17. Mixture of 11 and 2	
18. Mixture of 9 and 2	

TABLE 1 (Contd)

Fibre	Density g/cm^3	Medium	Method	Reference
Acrilan				
	1.17	17	E	44
	1.17-1.22	15	E	45
	1.176-1.232	15	E	49
	1.174-1.189	15	E	24
Cellulose acetate				
	1.30	17	E	53
	1.31	17	E	42
Cotton				
	1.534	2	A	21
	1.536	17	E	44
	1.538	17	D	51
	1.541	17	E	51
	1.542	3	B	13
	1.544-1.562	12	D	23
	1.547-1.553	17	D	1
	1.550	17	E	53
	1.550	17	E	42
	1.550	9	A	5
	1.554	1	B	13
	1.610	10	A	5
	1.610	10	A	1
Nylon				
	1.140	1	A	55
	1.140	17	E	42
	1.141-1.146	13	E	15
	1.142-1.154	17	E	44
	1.150	17	E	53
	1.164-1.166	10	B	15

TABLE 1 (Contd)

Fibre	Density g/cm^3	Medium	Method	Reference
Polyethylene				
	0.92	17	E	42
	0.92	14	E	53
Polypropylene				
	0.906-0.914	16	E	44
Silk				
	1.34	17	E	53
	1.34	17	E	42
	1.353	1	A	56
	1.426	10	A	56
Terylene				
	1.38	17	E	53
	1.39	17	E	42
Tricel				
	1.28-1.29	17	E	53
Viscose Rayon				
	1.507-1.537	12	D	23
	1.518-1.525	2	D	1
	1.520	12	E	42
	1.520	12	E	53
	1.534	9	A	5
	1.608	10	A	5
	1.614-1.620	10	A	1
Wool				
	1.30	17	E	53
	1.30	17	E	42
	1.303	7	A	3
	1.304	1	A	3
	1.306	7	A	3
	1.319-1.323	12	E	43
	1.394-1.397	10	A	3
	1.396	4	A	3
	1.408	6	A	3

3. EFFECT OF TEMPERATURE

Russell and Van Kerpel[52] studied the effect of temperature on specific volume of dry cellulose acetate and triacetate, and calculated the volume coefficent of expansion. They found that there was an increase in the coefficient with an increase in temperature, and hence a decrease in density. Hunter and Oakes[54] using a dilatometer made a through study of the effect of temperature on the density of polyethylene. They found that about 55% of the specimen was crystalline at room temperature and this fraction remained unchanged up to about 70°C, but thereafter fell rapidly until the specimen was completely amorphous at a temperature between 100°C and 120°C depending on the nature of the substance. They explained that the density of molten polyethylene was only slightly dependent upon average molecular weight, but the temperature at which crystalline material first appears on cooling was raised by an increase in molecular weight. The curve for polyethylene fibre showed a decrease in density with an increase in temperature.

Juilfs[53] studied the density of dry viscose rayon at 10°C intervals of temperature from 20°C to 70°C. A gradient column filled with xylene and

carbon tetrachloride was used, the density of the fibre decreasing up to 35°C and then increasing from 35°C to 70°C. Temperature and humidity might be expected to have a combined effect on the density of a fibre, a rise or fall in temperature causing a fall or rise in humidity causing a fall or rise in regain. The resultant density would appear to depend on the relative rates of temperature and regain effects.

4. EFFECT OF REGAIN AND HUMIDITY

It would be expected that any factor which influenced the mass or volume of a fibre, would affect the value of density. Many fibres absorb water from the surrounding atmosphere resulting in increased weight and volume and hence the change in density will depend on the relative rates of change of these two quantities.

Hermans[1] studied the effect of regain on density of viscose rayon filaments. He explained that the initial increase of density with regain was due to the existance of free space inside the fibre, being first occupied by water molecules, thereby increasing the weight of the material without adding to the volume. After the free space was fully occupied an increase

in volume due to swelling overtook the increase in mass due to moisture absorption, resulting in a fall of density until saturation was reached.

Stamm and Seborg[54] determined the density of native cotton at various regain, and showed that the curves ran through a maximum value which corresponded to a lower water content in native cellulose than in the regenerated cellulose. They considered that the initial increase in density depends on the contraction resulting from water absorption which used to be ascribed to compression of the water in the pores of the material.

Speakman and Saville[55] showed that the density of nylon like that of wool fibre, first increased, and then decreased with the increasing water content, but the maximum density was attained at a higher humidity than viscose rayon.

In general, a characteristic feature of all the curves obtained for different fibres such as cotton[5], silk,[56] and wool[57] is the initial increase in density which accompanies the absorption of small amount of water, followed by a fall in density as more water is absorbed. It follows that changes in the value of the density of a hydrophilic fibre may be expected with changes in the relative humidity of the

atmosphere. Sorption[58] may be defined as the process in which vapour molecules are attached to sites in solids.. Moisture sorptions occur mainly in the non crystalline regions of the fibres, and it has been reported[59] that the amount of water absorbed at a given temperature and humidity is proportional to the amorphous fraction sharing of one molecule by two or three sorption sites, (known as co-operative sorption).[60] Various authors have reported[61-66] the theoretical deductions based on the concept of multi-layer sorption in fibres to explain the observed sorption isotherms. Fig.1. shows the sorption isotherms of a number of textile fibres, the order of change in the density with humidity being expected to be greatest with fibres with the steepest gradient such as viscose rayon and wool, and less with Terylene and Acrilan while no change at all would be expected with completely hydrophobic fibres such as the polyolefines.

5. ASPECTS OF DENSITY MEASUREMENT

General aspects that require consideration include the amount, cleanliness, and condition of the fibre; the speed, accuracy, and ease of measurement of the test methods; and the problems of fibre diameter and liquid media which influence the determination of

real and apparent density.

The fibre must be clean and measurements made at known values of temperature, humidity, and regain and ideally a method for measuring the density should be capable of dealing with a single fibre, but instances could occur where measurements based on a cluster of fibres were required. Some comments have already been reported on the speed and ease of measurement of the different methods and opinions seem to be divided on whether the specific gravity bottle method or the flotation method provides the greater sensitivity and accuracy. Campbell and Russell[16] in their studies of the density measurement of cellulosic fibres reported that by specific gravity bottle the density could be obtained to an accuracy of 0.01 g/cm^3, while Hermans[67] reported in his studies of the density of viscose rayon that by flotation method the density could be obtained to an accuracy of 0.001 g/cm^3. For general comparison between materials the former would appear sufficient but the latter would be required to measure the differences between modified fibres of the same origin.

Some comment may be made on the influence of fibre structure and liquid media on density. A study of the morphological structure of cellulose fibres has suggested that they may contain pores, the

dimensions of which are far larger than the dimensions of most of molecules,[68-70] and that the density and the specific volume of a substance are typically macroscopic physical constants. If the density of a porous body must be determined by means of a submersion in a liquid or a gas, the following cases may be determined.

(1) The medium does not penetrate into the pores at all. The volume measured is the external volume and the reciprocal value is the so called apparent density of the porous body.

(2) The medium only partly penetrates into the pores. The density found is greater than that in the first case, but lower than the true density of the compact material.

(3) The medium fills all the pores completely, giving the density of the compact substance.

(4) The medium penetrates into all the pores and is moreover compressed giving a higher density. The value found for the density of the substance will then be too great.

Hermans[71-72] attempted to evaluate the ratio of crystalline to non crystalline cellulose in several fibres, and assumed that the lower density was due to interchain spaces in non crystalline regions, and also confirmed that the density measured in various media

depends on the nature of these media. According to Hermans,[22] the volume of a porous body could be measured only using the molecules that are considerably smaller than the dimensions of the pores in the body. Since the density of fibres in benzene, carbon tetrachloride, toluene and similar non swelling liquids was the same, although the size of these molecules varies, this density may be regarded as the macroscopic density of the fibre. This macroscopic density was regarded by Hermans as the real density of the material.

Thus it seems reasonable to conclude that the density of the fibre could be measured only by using organic liquids, such as xylene, toluene, benzene, carbon tetrachloride, pentachlorethane and n-heptane.

Reasons for measuring fibre density

The density of a fibre is one of the fundamental properties of the material. Its value depends on the chemical constitution and on the physical distribution of the atoms and molecules within the fibre. Thus a knowledge of the density value for a particular fibre serves as a means of identification, while the range of density affords information on the structure and modifications of a particular fibre.

Density is also related to the properties of the fibre; the effect of heat and light, stress-strain characteristics, weight and dimension, swelling and solubility being some of the items that have been considered.

Density was considered by Speakman and Saville[55] when they measured the stress-strain relationship of nylon at different relative humidities. Flory[73] studied the macromolecular structure and mechanical properties of fibrous proteins and stated that the dimensional changes brought about by heat and other agencies could be explained by the melting of crystalline regions. He pointed out that the crystalline structure of the fibrous protoins differed from that of the synthetic polymer, being imposed upon the structure which was in a highly ordered state, whereas in synthetic materials, cooling of the melt leads to a dispersion of small crystalline nodes.

Hermans[22] studied the relationship between the density, molecular orientation and swelling of treated viscose rayon filaments. He found that the acid catalyst used in the process may affect the physical properties of the treated fibres, and concluded that orientation was unaffected but that differences in swelling were uncertain. He further stated that

the fibre substance must be considered as compact and consisting of a practically homogeneous mixture of crystalline and amorphous parts. It would also be expected that there was a definite relationship between refractive power and density of the fibre. This has been illustrated by the Gladstone and Dale rule which states that if n be the refractive index of a substance and d the density, then $\frac{n-1}{d}$ is a constant value for a given fibre, from which by multiplication by the molecular weight M, the molecular refraction (MR) of the substance may be obtained.

Cooke and Warwicker[74] stated that the density of any partially crystalline lattice will be less than that calculated for the crystalline lattice, and density measurements were used to investigate changes in the crystallinity of viscose fibres during spinning when the density tended to increase, and hot extrusion treatment when the density tended to decrease.

CHAPTER 11 : EXPERIMENTAL METHODS

1. MATERIALS AND CHEMICALS

Materials.

Details of the fibres used in the present investigations. have been given in Table 2.

TABLE 2

Fibre details

Acrilan[3.4.]	fibre,	377	millitex,	5"-15" staple
Cellulose acetate[3.4.]	yarn,	111	millitex,	1 7/16" staple
Nylon[5] 66	yarn,	250	tex,	1 fil
Polypropylene[1.2.]	yarn,	22	tex,	40 fil
Polyethylene[1.2.]	yarn,	32	tex,	1 fil
Polyurethanes				
Chemstrand[1.2]	yarn,	46	tex,	1 fil
Glospan[1.2]	yarn,	62	tex,	1 fil
Lycra[1.2]	yarn,	51	tex,	1 fil
Spanzelle[1.2]	yarn,	46	tex,	1 fil
Vyrene[1.2]	yarn,	50	tex,	1 fil
Terylene[3.4.78.]	yarn,	17	tex,	48 fil
Tricel[3.4]	fibre,	136	millitex	1 7/16" staple
Viscose rayon[6.7.8.9.] (normal filament)	yarn,	186	millitex	1 7/16" staple
Viscose rayon (modified)				
Bright Fibro[1]	yarn,	111	millitex,	1 7/16" staple
Durafil[1]	yarn,	166	millitex,	1 7/16" staple
Strong Fibro[1]	yarn,	111	millitex,	1 7/16" staple
Vincel[1]	yarn,	166	millitex,	1 7/16" staple
Viscose rayon[1] (resin treated)	yarn	30	tex (fibro)	-
Cellulosic film[1]				

Key:- (1) Dry state at 20°C
(2) Temperature experiments
(3) Dry and humidity experiments at 20°C
(4) Temperature and humidity experiments
(5) Mass per unit volume experiments
(6) Specific gravity bottle
(7) Flotation method
(8) Density gradient column
(9) Beckman method.

Chemicals:

All liquids were Analar quality and were dried before use where necessary. Table 3 shows the liquids used and Tables 4 and 5 show the high and low density liquids used for density determinations at different regains and temperatures for various fibres.

TABLE 3

Selection of pure liquids.

Liquids	Density (20°C) g/cm^3
Carbon tetrachloride	1.595
Pentchloroethane	1.673
Xylene	0.864

Table 4

Densities of mixtures of xylene and carbon tetrachloride for dry/humidity density measurements. (20°C)

Fibre	Low density g/cm^3	High density g/cm^3
Acrilan	1.123	1.256
Cellulose acetate	1.262	1.385
Nylon	1.104	1.224
Polypropylene	0.864	1.106
Polyethylene	0.864	1.106
Silk	1.294	1.410
Terylene	1.335	1.455
Tricel	1.230	1.355
Viscose rayon	1.478	1.595
Wool	1.262	1.385

TABLE 5

Densities of mixtures of xylene and carbon tetrachloride for temperature/humidity measurements. (20°C)

Fibre	Low density liquid g/cm^3	High density liquid g/cm^3
Acrilan	1.123	1.305
Cellulose acetate	1.262	1.422
Nylon	1.104	1.276
Polypropylene	0.864	1.155
Polyethylene	0.864	1.155
Silk	1.294	1.455
Terylene	1.335	1.510
Tricel	1.230	1.402
Wool	1.262	1.422

Where dry liquids were used for density measurements, xylene was dried over sodium wire[75] and redistilled, and carbon tetrachloride and pentachloroethane were dried over calcium chloride[76] and potassium carbonate,[77] respectively and redistilled. The density of each liquid was obtained by specific gravity bottle measurements, and was checked by the appropriate specific gravity hygrometer. The volume addition property of each combination of low and high density liquids was also checked.

2. CLEANING, DRYING, CONDITIONING, AND PREPARATION OF SAMPLES.

Cleaning

All samples other than those mentioned below were purified with ether, washed in 1% Teepol solution at 60°C for 15 minutes, rinsed with distilled water, dried and conditioned in humidity room at 65% relative humidity and at 20 ± 1°C, for 48 hours, and were tested under these conditions.

Wool: Wool fibres from a Lincoln fleece, were cleansed by steeping in petroleum ether for 24 hours, given a soxhlet extraction with methylene chloride,[3] and then washed in 1% Teepol solution at 60°C for 15 minutes, being finally rinsed with distilled water. The fibres were dried, conditioned at 20 ± 1°C, 65 ± 1% r.h:. and stored in closed containers. The root and tip portions of a fibre were removed before use. Merino fibres were similarly treated.

Nylon 66: 2.22 tex bright monofilament nylon was cleaned by extraction with alcohol and ether,[55] followed by washing and drying as wool.

Silk: Silk yarn was purified by immersing for 1 hour in 1% Teepol solution at 98°C, rinsed in 0.5% soap solution at 98°C rinsed in hot 0.6% ammonia solution, rinsed, extracted in a soxhlet successively with alcohol, then ether and again with alcohol,[56] rinsed thoroughly in water, allowed to soak in water at 50°C, for 1 hour and finally dried in humidity room at 65% relative humidity and at 20° ±1°C for 24 hours.

Viscose rayon: Samples of viscose rayon yarn were extracted with methylene chloride and alcohol,[22] followed by washing and drying as wool.

Drying

For tests on dry fibres the method of drying recommended by Hermans[22] was used. Fibres were exposed for 12 hours in an oven at 105°C and then kept at 20°C in a vacuum desiccator over phosphorus pentoxide until required.

Conditioning

For tests requiring regain or relative humidity conditions dry fibres were transferred to a desiccator at 20°C under the appropriate desired relative humidities obtained by the use of saturated salt

solutions shown in Table 7, and kept until required. For experiments involving temperatures above 20°C the samples (and desiccator) were kept in an oven at the required temperature for several hours.

Preparation of samples

Samples were usually rolled between gloved thumb and forefinger to form small loosely packed, spherical pellets with a diameter of 2 to 3 mm, and a weight of 0.5 mg. In the case of density measurement of dry fibres, two different methods were used to expel air from fibres before placing them into gradient column.

Method A: Fibres were boiled in xylene for three minutes and then rapidly transferred to the gradient column.

Method B: A technique similar to that used by Hermans[22] was employed. The apparatus being shown in Figure 2(a). The outlet tube 7 was connected to a water pump. Samples after drying at 110°C were suspended in vessel 4, which was kept at 40 - 45°C by placing the vessel in a beaker of water, and kept under vacuum. Carbon tetrachloride in 1 was boiled at 35°C under reduced pressure and by opening tap 3

the vapour expelled all the air from the vessel 4. After 30 minutes stopcock 6 and tap 3 were closed, and the heating bath at 1 and 4 were removed and the flask 1 lifted to a horizontal position so that on opening tap 2, vessel 4 was filled to the top with air free carbon tetrachloride from which the sample could be transferred to the gradient column as required.

It was found that the density of the fibre after this treatment was the same as that after boiling the fibre in xylene and hence Method A has been preferred on grounds of speed and simplicity.

3. MEASUREMENT OF DENSITY

(i) Mass per unit volume

(ii) Specific gravity bottle.

(iii) Flotation method

(iv) Density Gradient column

(v) Beckman method.

Mass per unit volume

Lengths of high tex monofilament nylon fibres were available and inspection showed that they possessed a relatively smooth and circular section. 5 cm lengths were cut, cleaned and dried. Individual

lengths were measured with a cathetometer to 0.001 cm, weighed to 0.0001 g, and five readings of diameter taken to 0.0001 cm.

Assuming complete circularity then,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{Mass}}{\pi d^2 h/4}$$

where d = fibre diameter cm.

h = fibre length cm.

The means of ten observations were taken and density determined with an accuracy of $\pm$ 0.01. g/cm^3

Specific gravity bottle method

Density determinations for wool and viscose rayon were made using the specific gravity bottle method.[55] A specific gravity bottle, containing a known weight of fibre was filled with water, air bubbles being removed by stirring with a glass rod, followed by a brief reduction in pressure by placing the sample in a sealed desiccator under vacuum condition. The bottle was then transferred to a water thermostat at 20^{0}C, equilibrium being attained in one hour, weighings being repeated until a constant reading was obtained. The weight of specific gravity bottle with distilled water at 20^{0}C had previously been determined and hence the density of the fibre

could be calculated. The means of five observations being taken and density determined with an accuracy of ± 0.0005. The experiment was repeated using xylene, and carbon tetrachloride in place of water.

Flotation method

Density determinations for nylon, Terylene wool and viscose rayon were made using flotation method.[51] Small samples of fibres were chopped up to 1 mm lengths, boiled in xylene and placed in a 15 ml centrifuge tube containing a mixture of carbon tetrachloride and xylene of the approximate density to that of the fibre. Centrifuging was carried out for two minutes at 2000 r.p.m. and the density of the liquid adjusted until the fibres just remained in a state of suspension. The value of this density of the liquid was obtained by pycnometry and taken as the value of the density of the fibre. Five readings per sample were taken and it is considered that the method gave values to an accuracy of ± 0.0005

Density gradient column

Method A: A density gradient column was initially prepared in a 500 ml stoppered measuring cylinder[42] graduated in 5 ml division. To 250 ml of carbon tetrachloride was added successive amounts of the

lighter liquid xylene, the column after being gently stirred for 10 seconds after filling, was left in a conditioned laboratory at 20 $\pm$ 1°C, for 48 hours before use. Gradients prepared in this way were found to be stable for three weeks. While the approximate density at any level in the column can be calculated, the gradient columns were calibrated using a series of glass beads of known density so that an accurate density profile could be obtained. The densities of the beads had been determined by Archimedes principle. The calibration beads after drying in acetone were introduced into the gradient column and their position noted by means of a cathetometer. Readings were taken at a point threefifths of the way down the bead, experiments having shown that this was a fair approximation to the centre of gravity of a bead as constructed. Viscose rayon, wool, nylon and Terylene fibres which had been rolled into a small bead after preparation were gently inserted in the gradient column, and a period of one hour allowed for equilibrium. Their positions were then noted by means of a cathetometer or by reference to the volumetric scale, and the density obtained by reference to the calibration curve for the column. The use of a cathetometer minimised the risk of error due to inaccurate reading of the position of the sample.

Method B: As mentioned in the introduction, refinements in the methods of preparing gradient columns have been suggested and that by Jones[78] has been used. The apparatus, shown in Figure 3, consists of a jacketed column D, mixing chamber B, and a open container A, connected through cocks G and H as shown. The magnetic stirrer C was situated below the mixing chamber B, and the glass unit connected to the vacuum pump when filling the column.

The empty column was subjected to reduced pressure and the low density liquid drawn through cock H, and replaced in the chamber by high density liquid from the beaker. A gradual and even increase in the density of the liquid in the chamber, and therefore of the liquid drawn into the column, was ensured by continuous mixing of the liquid in B with an electromagnetic stirrer. When the column was filled cock H was closed and the column was ready for use. The time taken to establish the column was about 15 minutes. The liquid column could be kept in a dry condition by using a dehydrating head, and the temperature controlled by circulating water from a thermostatically controlled water bath. One difficulty that was not overcome was that mixing of the liquids did not begin immediately with the result that (pure) low density liquid was drawn into the

column. The height or volume of this had to be allowed for in any calculations or measurements involving reference to the top of the column. The density at any point below the top of the column may be calculated from the following formula,

$$P_h = e^{-Ah/v}$$

Where P_h = proportion of the original low density component in the solution. h = height at a point from the top of the column. (cm). A = cross sectional area of the column. (cm^2). v = volume of the low density liquid in the chamber. (cm^3). For the sake of convenience the tube was graduated volumetrically and filled with same volume of the liquid on every occasion, so that the volume of the liquid above each of the graduations then being known, the calculations of the density profile was simplified. Table 6 shows the relationship between this ratio and the density of the liquid at any level. It follows that one method of obtaining the greatest sensitivity over a small range of density is to keep the ratio small (large value of v) and to select a low and high density liquid as near as possible to the expected density of the fibre. If however low and high density liquids are too close together in density value then some difficulty

may be experienced in differentiating the initial and final changes in density in the column. A density profile (calculated) for a column where Ah = 1000 ml, v = 1000 ml, low density liquid 1.250 and high density liquid 1.450 is shown in Figure 4, where the ratio Ah/v is equivalent to successive heights of 100 ml. The accuracy of the method depends on the accuracy of the determinations of the original liquid densities and of the measurement of the (volume) height at any specific point in a column. It is thus an advantage to have as narrow a column as possible within the limitations imposed by ensuring freedom of sample measurement. The means of ten observations were taken and density determined with an accuracy of $\pm$ 0.0005.

The density gradient column was checked by the use of glass beads which were prepared to cover the range of densities involved. The (experimental) profile of the calibrated glass beads are also shown in the Figure 4, and the density of a sample could be obtained from a curve or by interpolation by finding its height in the column. The equilibrium time of fibres in gradient column have also been shown in Figure 5. Columns which cover a wide range of density are relatively less sensitive to fluctuations in temperature, but have an increased tendency to diffuse, and hence the coarser columns are less stable and less

durable than the finer ones. The finer gradients were found to be stable for five weeks or longer, the period for the coarser gradients being about three weeks.

TABLE 6

Effect of height on proportionality of low and high density liquid in gradient column.

Height h 'ml'	Ratio Ah/v	Proportion of low density liquid	Proportion of high density liquid	Density g/cm^3
100	-.1	0.905	0.095	1.270
200	-.2	0.818	0.182	1.284
300	-.3	0.741	0.252	1.302
400	-.4	0.670	0.330	1.316
500	-.5	0.607	0.393	1.329
600	-.6	0.549	0.451	1.340
700	-.7	0.485	0.515	1.353
800	-.8	0.449	0.551	1.360
900	-.9	0.406	0.594	1.369
1000	- 1.0	0.368	0.632	1.376
1500	- 1.5	0.224	0.776	1.406
2000	- 2.0	0.136	0.864	1.423

v = 1000 ml

Construction of glass beads.

The construction of glass beads of particular density was facilitated by the following relationship. Assume a bead to consist of a hollow cylinder and whose ends are rounded and sealed such that together they would be equivalent to a sphere and let the length of the cylinder be 1 cm, the inner axial radius be r_1 cm, and the outer axial radius be r_2 cm;

then, Volume of the bead = $\pi r_2^2 \ell + 4/3\pi\ r_2^3$ c.cm.

and, Mass of the bead =

$$\pi(r_2^2 - r_1^2)\ell\rho_g + 4/3\pi\ (r_2^3 - r_1^3)\rho_g \text{ (approx)}$$

so that, Density of the bead $\frac{\text{Mass of bead}}{\text{Volume of bead}}$

$$\rho = \frac{\rho_g\left[1-\left(\frac{r_1}{r_2}\right)^2\right]\ell + \frac{4}{3}r_2 - \frac{4}{3}r_1\left(\frac{r_1}{r_2}\right)^2}{\ell + \frac{4}{3}r_2} \quad \text{(A)}$$

$$\rho = \rho_g\left[1-\left(\frac{r_1}{r_2}\right)^2\right] \qquad \text{Approx if wall is thin, } r_1 = r_2 \text{ ... (B)}$$

where ρ_g is the density of glass.

Effect of length on the density of bead:

Assuming ℓ = 10 mm, applying this to equation (A)

$$\rho = \frac{2.5 \left\{[1 - 0.48]\ 10 + \frac{4}{3}\ .2 - \frac{4}{3}\ .1.386\ .0.48\right\}}{10 + \frac{4}{3}\ .2}$$

$\rho \doteq 1.38$

This seemed to be near enough 1.3 in view of the approximation made, if ℓ = 20 mm, then, ρ = 1.34. i.e. ℓ has only a second effect on the density of the glass bead, so that the density of the bead depends mainly on the ratio of the internal to external diameter and on the density of the glass of which it is made. By taking tubing of different suitable thickness the theoretical density of various glass beads was calculated, after applying the value of $r_1 = r_2$ in the equation (B).

Finally the above beads were calibrated for their correct density which is given by,

$$\text{Density of bead} = \frac{M_a}{M_a - M_w}\ g/cc.$$

where M_a = weight of bead in air,

M_w = weight of bead in water.

Beckman method

Density determinations for wool, viscose rayon, nylon 66, and a blend of wool and viscose rayon fibres were made using a Beckman air comparison pycnometer which uses a principle of volume comparison. The weight of a material being known the volume is obtained by measuring the loss of air space in a cylinder containing the material compared with the volume of the (empty) cylinder containing air only.

A simplified schematic diagram, shown in Figure 2(b), consists of Purge valve A, Coupling valve B, Reference piston C, Measuring piston D, Sample cup E, Differential pressure indicator F, and Counter G. Before taking sample measurements, zero measurements were checked by using clean sample cup (to compensate for possible zero error.) When the zero counter reading was greater than zero, it was used as a tare number and subtracted from the subsequent sample volume measurements, and when the zero counter reading was less than zero the difference between the reading and zero was added to subsequent sample measurements. The calibration of the pycnometer was checked by measuring the volume of two stainless steel test spheres, supplied with the instrument, the means of ten observations being taken and the volume obtained to an accuracy of $\pm$ 0.010 g/cm^3.

The operation of the instrument depends on the fact that the rate of expulsion of air from the cylinders 1 and 2 must be kept the same by keeping the pressure differential at zero, and assuming the same cross-sectional area for both cylinders. The volume swept by the piston in an empty chamber is the product of the area of the chamber and the distance moved by the piston, with a sample in the chamber the free volume of the chamber is reduced by an amount equal to the volume of the sample. The area of the chamber has not been altered and hence the reduction in volume is proportional to the reduced sweep of the measuring piston. The principle of the instrument therefore is to obtain a measurement of volume by observing a change in linear displacement. The same is true if the air in the chambers is not allowed to escape but is compressed (or expanded) as long as the pressure differential between the two cylinders remains zero, and the normal procedures involve an increase or decrease in pressure by a factor of 2. Moisture and temperature changes during a test are two items which require attention.

Sample measurements were made using three different methods.

(a) Atmospheric operation 1 to 2

(b) Atmospheric operation 1 to 2
(Moisture allowance)

(c) Atmospheric operation 1 to ½ to 1

(a) Atmospheric operation 1 to 2

With the purge valve closed and the coupling valve open the reference hand wheel and measuring hand wheel were rotated to the extreme counter clockwise position, then the measuring hand wheel was turned to the clockwise position until the starting number was set on the counter. The starting number, 1082 in this instance, is the total volume of the cylinder swept by the piston. A sample of known weight was placed in the cup, inserted in the compartment, and locked by pressing clamp handle firmly down. After 15 seconds the coupling valve was closed and both the wheels were rotated simultaneously clockwise until the reference hand wheel rested firmly against the stop. During this operation care was taken to keep the pointer on the scale, and after 10 seconds the pointer was brought to zero with the measuring handwheel, the coupling valve was opened and

the sample volume was read on the counter. The mean of ten readings were taken and the density measured to an accuracy of $\pm$ 0.01 g/cm^3.

(b) Atmospheric operation 1 to 2 (Moisture Allowance)

It had been suggested that moist fibres might cause a shift in the zero tare if moisture was allowed to reach the reference cylinder, or remain in the measuring cylinder from one determination to the next, and hence volume determination was made as follows.

After the sample had been placed in the compartment and locked the coupling valve was closed immediately, then both hand wheels were turned simultaneously until the reference hand wheel rested against a stop. The null point was brought to zero with measuring hand wheel, the coupling valve was opened and sample volume on counter was read directly. Immediately after confirming the null point the coupling valve was closed and the hand wheel was rotated counter clockwise to the starting position and the sample was removed. Before opening the coupling valve the measuring cylinder was swept free of excess moisture, by moving the measuring piston in and out a few times with the measuring hand wheel. The mean of ten

readings were taken and the density measured to an accuracy of $\pm$ 0.01 g/cm^3.

(c) Atmospheric operation 1 to $\frac{1}{2}$ to 1.

With the purge valve closed and the coupling valve opened the reference hand wheel was rotated to clockwise forward stop position, and the measuring hand wheel was rotated to the estimated sample volume. The sample and cup were placed in the compartment, locked and the reference hand wheel rotated counter clockwise to its rear stop, and the measuring hand wheel rotated counter clockwise, to a point beyond starting number and then clockwise to the starting number. After 10 seconds, the coupling valve was closed and both the hand wheels rotated simultaneously until reference hand wheel rests against stop. During this process the pointer was kept on the scale. Again after 10 seconds the pointer was brought to zero with measuring hand wheel and the coupling valve opened and sample volume was read. The mean of ten readings were taken and the density measured to an accuracy of $\pm$ 0.01 g/cm^3.

4. MEASUREMENT OF REGAIN.

For the determination of moisture regain in fibres a simple method was employed,[22] small samples (0.5-1/g) were transferred to small dry ground glass weighing bottles, and dried in an oven at 105°C for 12 hours till constant weight, then dried over phosphorous pentoxide in vacuo at room temperature 20 ± 1°C for 24 hours. The sensitivity of the balance was 0.0002 g and hence their dry weight was determined with an accuracy of better than 0.1%. These samples were kept for 24 hours till constant weight, in sealed desiccators at various relative humidities, obtained by the use of series of saturated salt solutions, prepared at 20°C, and their regains were calculated. High vacuum Silicone grease was used to ensure a vacuum tight seal between the free end of the rubber tubing. Table 7 shows the various saturated salt solutions which were used in the present work with their expected relative humidities[89]

TABLE 7

Selection of salt solutions with their appropriate relative humidities (20°C)

Saturated salt solution	Relative humidity (%)
Phosphorus pentoxide	0.0
Potassium acetate	20.0
Calcium chloride	32.3
Sodium dichromate	52.0
Sodium nitrite	66.0
Ammonium sulphate	81.0
Ammonium dihydrogen ortho-phosphate	93.1
Copper sulphate	98.0

5. EFFECT OF TEMPERATURE

One part of the present work was concerned with the measurement of the density of fibres at temperatures other than 20°C, and hence it was necessary to check the effect of temperature on the method. The densities of the glass beads used for calibrating the density gradient column were measured at temperatures of 20°C, 30°C, 40°C and 50°C. It was found that the density of the glass beads did not change with an increase in temperature. This might be

expected as the coefficient of thermal expansion of Pyrex glass is very small being 0.033×10^{-4} in the temperature range from 21° - 330°C.

For measuring the density of fibres at higher temperatures than 20°C, the density gradient column was filled by taking the various proportions of the low and high density liquids, which have been shown in Table 5. The column was usually maintained at 20°C, an immersion thermometer (0° - 100°C) being inserted in the column to record the temperature. The temperature of the column was maintained by circulating water through the outer jacket from a controlled water bath. Small samples of dry fibres, prepared as previously described were introduced into the gradient column, and their equilibrium position was noted. The temperature of the column was then raised to the next higher temperature, usually by 10°C stages, and maintained till the fibres reached their new equilibrium position usually after 30 minutes. With higher temperatures, the samples did not attain an equilibrium position and the gradient was rapidly destroyed and hence for studying the density of viscose rayon at various temperatures pentachloroethane (b.p. 163°C) was used instead of carbon tetrachloride.(b.p. 76°C).

The density profiles for the column at temperatures 20°C, 30°C, 40°C,.....70°C, have been shown in the Figure 6 These tests were repeated with fibres conditioned at 66 percent relative humidity. The general procedure was the same as described for determining the density at zero percent relative humidity. The effect of temperature at any constant humidity could therefore be studied once the density profile had been established. The mean of five observations was taken and the density was determined with an accuracy of ± 0.0005.

6. EFFECT OF REGAIN AND HUMIDITY

For measuring the density of the fibres with moisture regain the gradient column was filled by taking the different proportion of the low and high density liquids, which have been shown in Table 4. Samples at various regains were transferred to the gradient column and the density measured in the usual manner. The anhydrous drying head containing phosphorus pentoxide at the top of the column being replaced with the appropriate saturated salt solutions. The mean of five observations was taken and the density was determined with an accuracy of ± 0.0005.

7. FRACTIONAL DISTILLATION UNIT:

In order to reduce the cost of liquids, the distillation apparatus shown in Figure 7 was used for fractional distillation of liquids at atmospheric pressure. It consists of support ring HR, locating ring LR, thermometers Th_1 and Th_2, grease tap T1, special ring RR, taps T2 and T3.

To assemble the apparatus all ground joints, tap keys, and barrels were wiped out with a clean cloth. The position of the heater jacket support ring, was adjusted so as to leave sufficient room below it to accommodate the distillation flasks. The heater jacket was mounted on the support ring with the 2 pin connector towards the front and located in a vertical position by means of the located ring into which fits the loose asbestos cement collar, found on the heater jacket. This locating ring was fixed in position about two thirds the way up the vertical lengths of the heater jacket.

For calibration, the heater jacket was wound with nickel-chrome tape which was terminated by the 2 pin plug. This was connected to the mains supply through a rheostat used to control the current passing through the tape and thus the temperature of the jacket. For this purpose the following arrangements were made.

The filled column was placed in the heater jacket by lowering it through the hole in the top of the jacket until it rests suspended by the lip of the upper ground joint. The distillation flask was attached to the lower end of the column and clamped it into position and the still head was fitted into the top of the column. The thermometer Th_1 was suspended in the jacket adjacent to the column. The heater jacket, rheostat and an ammeter was connected in a range 0 - 1.5 A. The resistance was adjusted until the meter indicates current in the order of 0.5 A., and it was left for three hours, until the thermometer Th_2 indicates an equilibrium temperature and at this point the current and temperature were noted, the current was then raised to 0.75 A. The readings were taken at four different current values, after determining the equilibrium temperature corresponding to the different currents and a graph was plotted within reasonable limits, to indicate the current necessary to maintain the jacket at any desired temperature and the value of the current flowing in the circuit for any given setting of the resistance was fmarked on cardboard scale and fixed alongside the resistance slider rod. By this device the need of the ammeter in the circuit was

obviated as the resistance was set by reference to the scale to give any desired current and hence any desired temperature of the heater jacket.

A 250 cc distillation flask was filled with the liquids to be distilled, attached to the lower end of the column and clamped in position. The various ground joints were greased. A 0^{o} - 330^{o}C thermometer was fitted through the B 1/4 thermometer tube of the still head by means of a piece of rubber tubing. The still head was fitted into the top of the column and the reflux condenser was fitted in position. The 250 cc receiving flask was fitted in position by using the specialsring RR, to support the flask. The calcium chloride tubes one at the top of the condenser and the other on the B1/4 joint above the receiver flask was fitted to avoid the presence of moisture, and the distillation was carried out to the desired temperature. The density of the distilled liquid was checked by using specific gravity bottle, and it has been found to be the exact density which should be for the required liquids.

CHAPTER III : RESULTS AND DISCUSSION

RESULTS AND DISCUSSION:

1. DENSITY OF VARIOUS DRY FIBRES

The density values of various dry fibres at 20 ± 1°C, obtained in a mixture of xylene and carbon tetrachloride by the gradient column method have been shown in Table 8. It is seen from these results that the difference in density values for different dry fibres reflects the major differences in fibre structure, and that slight differences exist between modified fibres of basically similar structure.

The values are in general agreement with those of Mikhailov[44] (acrylic, polypropylene), Preston and Nimkar[42] (nylon, cellulose acetate, silk, Terylene, viscose rayon, polyethylene), and Julfs[53] (silk, Terylene, Tricel, viscose rayon), whose results however were only given to ± 0.01 g/cm^3. Comments may be made on the results of Fortes[18] (celluloso acetate), Hurley and Tsentis[49] (acrylic), and Goodings and Turl[56](silk), as their results are higher than the present results.

Fortes[18] showed density values in different media ranging from 1.306 with carbon tetrachloride, 1.364 with benzene, 1.396 with ethyl alcohol to 1.415 with n-heptaldehyde, and suggested that density was influenced by the polar groups of the molecules of the liquid media and their size and shape. He

TABLE 8

Density of dry fibres (20°c)

Fibres	Density g/cm^3
Acrilan	1.174
Cellulose acetate	1.312
Nylon	1.142
Polypropylene	0.915
Polyethylene	0.927
Polyurethane	
Chemstrand	1.216
Glospan	1.275
Lycra	1.153
Spanzelle	1.265
Vyrene	1.322
Rubber	1.104
Silk	1.347
Viscose rayon (Medium tenacity)	1.525
Viscose rayon (Modified)	
Bright Fibro	1.507
Durafil	1.497
Strong Fibro	1.498
Vincel	1.509
Toryleno	1.384
Tricel	1.284
Wool	1.314

reported that the minimum density values found in carbon tetrachloride may be due to very little penetration below the cellulose acetate surface, while the higher value in benzene could be due to better penetration. This value was very close to the apparent density found in water where penetration involved association with the cellulosic hydroxyl groups.

The values found in ethyl alcohol and methyl alcohol were higher than water, this may be due to the hydrogen bonding of the alcohol hydroxyl group, coupled with the organophilic aliphatic group up to C_4 on the same molecule, which results in more effective penetration and solvation of the fibre than water or benzene alone.

Similarly the values of Goodings and Turl[56] for silk in benzene, and of King[3] for wool in methyl alcohol and ethyl alcohol are higher and this may be due to penetration into the fibre material as supported by Fortes.[18] Comment may be made in passing, that no difference in the density of Merino and Lincoln wool was recorded. The higher value for acrylic[49] fibres may be due to the void structure which can develop upon heating coagulated polyacrylonitrile, and which may be inaccessible to a surrounding liquid

but might be accounted for if any traces of moisture were present as the authors have not commented specifically on the dryness of these samples or solutions. Later work in this thesis illustrates this point. (Figure 10).

Ripa and Schneider,[50] discussed the density of acrylic fibres in organic liquids. According to them, liquid-polymer interaction and preferential adsorption in binary solution usually do take place e.g. carbon tetrachloride was preferentially adsorbed by polyacrylonitrile from a mixture of n-heptane and carbon tetrachloride, and hence the densities determined were those of the polymer-liquid compounds, and these apparent densities depend upon other factors, such as weight and dimensions of the adsorbed molecules also on the surface area of the polymer available for interaction.

No reference has been found for polyurethane fibres or for modified viscose rayon fibres. It has been stated that density values reflect modifications in a basically similar structure and this is shown by the values for viscose rayon. Fibro, Strong Fibro, and filament viscose rayon might be expected to show increased orientation and compactness of structure and the density values are in sympathy with this. In connection with the physically modified viscose rayons it may be noted that linear correlation was found between the relative accessibility

of the fibre and density.

Density and relative accessibility of viscose rayon fibres

Fibre	Relative Accessibility	Density g/cm^3
Bright Fibre	48	1.507
Strong Fibre	51	1.498
Vincel	47	1.509
Durafil	52	1.497

Relative accessibility in this case was arbitarily defined[98] as the ratio of the final tension after 20 hours stress relaxation to the initial (maximum) tension. The theoretical implications of the relationship have not been considered the illustration simply suggesting a possible application of density measurement effecting a considerable saving in time in routine measurement once correlation has been established.

It is interesting to note that the density values of polyurethane correlate with the Schwartz values found by Meredith and Fyfe,[79] which have been shown in Figure 18, while there is some correlations between density of polyurethane and the stress at 200% ext, also reported by Meredith and Fyfe[79]. Figure 19 shows a comparison between the polyurethane sample density and yarn stress

at 200% extension. The conditions marked 1 to 5 in Figure 19 were as follows. (1) tests at 20°C and 65% r.h. (2) tests at 20°C in water. (3) tests at 90°C in water. (4) tests at 20°C and 65% r.h. on samples preheated for 24 hours at 105°C. (5) tests at 20°C and 65% r.h. on samples preheated for 24 hours at 130°C. Both the Schwartz value and the stress at 200% extension may be regarded as tensile moduli reflecting the mechanical property of the yarn and would be expected to be influenced by the orientation and crystallinity of the fibre and the changes in these that occurs on stretching. Such differences in fibre structure would be expected to cause differences in the densities of the fibres and this has been found to be the case. For exact correlation values of density would require to be obtained on fibres tested under the same conditions as those appertaining to each tensile property. In the present case density was only measured on the unstretched dry fibre at 20°C but even so some correlation has been noted. The greatest variation has occurred with samples which have been heated for 24 hours at 130°C when any change in actual density would be expected to be greatest.

Consideration of the densities of dry fibres is continued in the next section.

2. COMPARISON OF TEST METHODS.

The densities of various dry fibres at 20°C obtained by using different methods and with different media have been shown in Table 9, and enables comparisons to be made.

The density values of nylon by mass per unit volume method compared by that obtained by other methods, shows that the method is feasible provided that the length, diameter and weight may be accurately determined. The method is thus limited to fibres possessing circular or uniform section and preferably in filament form. The accuracy is not high but is sufficient to enable the method to be used to identify the filaments of materials whose density values are known to differ by at least 0.01 g/cm^3. The values obtained by the Beckman method appear useful, but in fact there is no automatic end point to the experiment, which is therefore influenced very largely by a conscious knowledge of the correct or expected result. In other words the method can provide the correct answer on a material of (known) density but has not been found successful when dealing with unknown quantities. No significant difference in results was found between the three test methods in this instance, but this is probably due to the general variability of any one method and this would have been investigated more fully

TABLE 9

Comparison of test methods

Key:-

Methods: (1) Mass per unit volume.
(2) Specific gravity bottle
(3) Flotation,
(4) Density gradient,
(5) Beckman.

Medium used: B Xylene, C Carbon tetrachloride,
D Xylene and Carbon tetrachloride,
A Air, E Water.

Fibre	Method	Medium	Density g/cm^3
Nylon	1	A	1.15
Nylon	3	D	1.146
Nylon	4	D	1.142
Nylon	5	A	1.14
Wool	2	B	1.319
Wool	2	C	1.327
Wool	2	E	1.398
Wool	3	D	1.317
Wool	4	D	1.314
Wool	5	A	1.31
Viscose	2	B	1.528
Viscose	2	C	1.532
Viscose	2	E	1.616
Viscose	3	D	1.526
Viscose	4	D	1.525
Viscose	5	A	1.52
Terylene	3	D	1.387
Terylene	4	D	1.384

had experiments using the Beckman instrument been continued.

For any fibre it appears from the results that the method 2 gives a higher answer than the method 3. Similarly the method 3 appears to give a higher answer than method 4, but it is probable that the apparent difference between the methods is in fact due to the different media used. Inspection of Table 9 will show that the results for both wool and viscose rayon were greater in carbon tetrachloride than xylene. A mixture of these liquids was used in both the flotation and the density gradient methods, whereas only a single liquid was used in the case of the specific gravity bottle method. Both liquids were in fact used for viscose rayon where a slightly higher value was found using carbon tetrachloride. Finally a significant increase in the density of both wool and viscose rayon was found when water was the immersion medium.

Davidson[5] determined the apparent density of cotton and viscose rayon samples in acetone, chloroform, benzene, carbon tetrachloride, nitrobenzene, water and toluene. With these liquids other than water he obtained values which differed from one another by less than the experimental error in the determination. If it is true that fibres contain pore spaces of molecular dimensions, it should be possible with suitable immersion liquids to

obtain different apparent fibre densities for the same fibre and furthermore, the differences in density values so obtained should vary in a manner related to the sizes of the liquid molecules used but such differences were not observed by Davidson[5] because the liquids which he used were composed of molecules of approximately the same size. This fact was revealed by Wakeham[19] when he compared the sizes of some liquid molecules used in his density determination of cotton fibres. He pointed out that if the medium used has an appreciably larger molecules than those of the same size, then lower fibre density will be obtained.

The density values with xylene and carbon tetrachloride indicated no penetration into the fibre structure, and the molecules fill the fibre pores completely while with water a small completely hydrophilic and organophobic hydrogen bonding molecules will penetrate the fibre surface, probably through the mechanism of associating-dissociating intermolecular cellulose hydroxyl hydrogen bonds in viscose rayon, and into the carbonyl and amide group into the wool fibre. This would suggest that water gives high density.

In the case of water, Hermans,[22] has obtained a fairly reliable picture of the behaviour of cellulose towards water. According to him the density in water

should rise and fall with the percentage of the amorphous fibre substance.

Lauer[8] has argued that the vapour of carbon tetrachloride was slightly absorbed by cellulose fibres; from his graph it may be deduced that rayon would adsorb about 0.3 percent at saturation, and hence the difference between the density values in xylene and carbon tetrachloride in the specific gravity bottle method may be explained.

King[3] found the same phenomenon for wool in water, and in various organic media, the values obtained in water being higher than with organic media. This being in accord with the density values of Davidson[5] for viscose rayon. Larose[90] repeated the experiments of King and found that some of the values given by King were not reproducible and that values similar to that of 1.306 for dry wool in benzene were obtained with other agents. Comment might be made that Larose reported the value of density obtained by a hydrostatic balance to be some 3% higher than that obtained by the specific gravity bottle method.

The results of the flotation method give density values in the mixture of xylene and carbon tetrachloride as accurately as possible. According to our experience the specific gravity bottle method is not very convenient

for measuring density on microscale because besides requiring considerable quantities of the fibre materials the precautions to exclude traces of moisture and air lead to difficult and tedious manipulations. The present results are in accord with the results of Abbott and Goodings[15] for nylon, Hermans[22] for viscose rayon. Moll[21] on the other hand got lower density of viscose rayon, but this may be due to his technique which did not completely exclude traces of moisture.

3. EFFECT OF TEMPERATURE AND HUMIDITY

The density values of Acrilan, cellulose acetate nylon, silk, Tricel, Terylene, viscose rayon, and wool at a constant relative humidity of 0% and 66%, over a temperature range of 20°C to 70°C have been shown in Table 10. The effect of humidity and hence moisture regain on the same range of fibres has been investigated and the values of density at 20°C have been given in Table 11.

The percentage change in density with temperature and humidity was calculated based on the density of a dry fibre at 20°C, and the results for the different fibres have been shown in Figures 8-15.

TABLE 10

EFFECT OF TEMPERATURE ON DENSITIES OF SOME FIBRES

	ACRILAN		CELLULOSE ACETATE		NYLON		SILK	
TEMPERATURE	R.H.		R.H.		R.H.		R.H.	
°C	0%	66%	0%	66%	0%	66%	0%	66%
	DENSITY g/cm^3		DENSITY g/cm^3		DENSITY g/cm^3		DENSITY g/cm^3	
20	1.174	1.178	1.312	1.315	1.142	1.147	1.347	1.347
30	1.172	1.176	1.309	1.312	1.140	1.145	1.345	1.345
40	1.170	1.173	1.307	1.308	1.138	1.142	1.342	1.343
50	1.167	1.169	1.303	1.304	1.135	1.139	1.339	1.340
60	1.163	1.165	1.300	1.301	1.132	1.135	1.335	1.337
70	1.159	1.160	1.298	1.298	1.129	1.131	1.330	1.333

	TERYLENE		WIROOL		VISCOSE RAYON		WOOL	
TEMPERATURE	R.H.		R.H.		R.H.		R.H.	
°C	0%	66%	0%	66%	0%	66%	0%	66%
	DENSITY g/cm^3		DENSITY g/cm^3		DENSITY g/cm^3		DENSITY g/cm^3	
20	1.394	1.397	1.284	1.287	1.525	1.494	1.314	1.317
30	1.393	1.396	1.283	1.285	1.522	1.489	1.312	1.315
40	1.392	1.395	1.281	1.283	1.519	1.483	1.308	1.312
50	1.391	1.389	1.279	1.280	1.521	1.498	1.303	1.308
60	1.379	1.391	1.277	1.276	1.525	1.495	1.298	1.304
70	1.378	1.378	1.275	1.273	1.528	1.514	1.293	1.300

TABLE 11

EFFECT OF REGAIN ON DENSITIES OF SOME FIBRES (20°C)

	ACRILAN		CELLULOSE ACETATE		NYLON		SILK	
R.H.	REGAIN	DENSITY	REGAIN	DENSITY	REGAIN	DENSITY	REGAIN	DENSITY
%	%	g/cm^3	%	g/cm^3	%	g/cm^3	%	g/cm^3
0	0	1.174	0	1.312	0	1.142	0	1.347
20	0.35	1.175	1.24	1.314	2.42	1.144	4.67	1.351
32.3	0.51	1.176	2.54	1.314	2.94	1.145	4.99	1.350
52	0.71	1.177	4.18	1.316	3.75	1.146	7.06	1.349
66	1.42	1.176	5.66	1.314	4.83	1.147	9.99	1.347
81	1.77	1.176	7.43	1.312	5.69	1.148	13.12	1.344
93.1	2.51	1.174	10.02	1.310	8.79	1.146	18.76	1.337
98	2.74	1.172	14.37	1.306	9.62	1.145	23.42	1.330

	TERYLENE		TRIACEL		VISCOSE RAYON		WOOL	
R.H.	REGAIN	DENSITY	REGAIN	DENSITY	REGAIN	DENSITY	REGAIN	DENSITY
%	%	g/cm^3	%	g/cm^3	%	g/cm^3	%	g/cm^3
0	0	1.384	0	1.284	0	1.525	0	1.314
20	0.18	1.384	1.21	1.285	4.66	1.527	5.94	1.317
32.3	0.23	1.386	2.34	1.286	6.82	1.520	8.03	1.310
52	0.28	1.386	3.90	1.288	10.13	1.502	11.47	1.318
66	0.32	1.387	5.15	1.286	13.24	1.494	14.52	1.317
81	0.44	1.390	7.25	1.284	17.96	1.468	17.93	1.315
93.1	0.50	1.386	8.87	1.282	25.10	1.427	23.18	1.308
98	0.80	1.385	10.27	1.280	29.90	1.413	27.96	1.302

Effect of humidity

Examination of the results for humidity, regain and density show that there is an initial increase in density at lower humidities with the absorption of small amounts of water, followed by a fall in density at higher humidities, as more water is absorbed. Initially the change is such that the increase in volume is less than the increase in mass. As absorption proceeds the rate of increase in volume supplants the rate of increase of weight and hence the density decreases. Hermans[22] explained the phenomenon in terms of the fibre structure as follows. Initially the change is such that the increase in volume is less than the volume of the added water. Apart from the improbable suggestion that the absorbed water is compressed, this must mean that the water molecules are fitted closely into the fibre structure, with a more complete use of the space available. The close fitting is in accord with the view that the first water molecules are directly attached to the active groups in the fibre molecule. As absorption proceeds, the increase in volume becomes equal to the volume of the water added indicating that the water is packed in much the same way as in liquid water or ice.

and is merely spreading out the polymer structure. Second, there is the gradual decrease in density, as the temperature increases, and with much higher temperatures this phenomenon becomes more predominant.

All this cannot be explained by a single theory. A general qualitative view of these results shows the action of several mechanisms of absorption, and there are quantitative theories associated with every possible mechanism. These theories will throw light on a variety of points of view, and they will be discussed in detail in terms of the particular type of fibre, but the ideas will usually be applicable to other fibres as well.

It is seen in Fig. 8 - 9 that the densities of nylon and Terylene increase up to 81% relative humidity, and then decrease at much higher humidities. This is probably due to the fact that there are no active groups and bulky side groups in nylon and Terylene, and up to 81% relative humidity the absorbed water may have entered into the empty space present in the dry fibre, resulting in an increase in mass relative to volume and hence the density would increase. At high humidities further absorption would lead to swelling resulting in greater increase in volume relative to mass with a decrease in density. This is in accord

with Speakman and Saville.[55] The maximum density of nylon was found at much higher humidities compared with Teryleneʼ, it may be due to the difference between the two types of fibres and of course in keeping with the smaller swelling and greater crystallinity of nylon. It is seen from the Fig.10. that the density of Acrilan increases up to 66% r.h. and thereafter decreases at higher humidities. This is probably due to the fact that there may be comparatively strong attractive forces between neighbouring molecules, and because of the polar nature of the -CN groups, which attract water at higher humidities. One might expect a decrease in density once the water molecules are fitted closely into the structure with more complete use of the space available.

The density values for wool, silk and viscose Fig 11 - 13 shows slightly more predominant behaviour than nylon and Terylene. The density value increases up to 32.3% relative humidities and then it decreases at much higher humidities (i.e. from 81% to 98% it falls rapidly). This is thought to be due to the fact that all the natural, regenerated, animal and vegetable fibres contain within their molecules groups which strongly attract water. In cellulose, there are hydroxyl groups, to which water molecules can be attached by hydrogen bonds.

In the proteins, there are carbonyl (-c = o) groups. in the main chain, and other active groups in the side chains.

The same phenomenon have also been noted by Hermans[22] (viscose rayon), Goodings and Turi[56] (silk) and Warburton[57] (wool). In the case of cellulose acetate, and Tricel (Fig 14 - 15) the density increased up to 52% relative humidity and then decreased. This may be due to that there are no active groups in the molecules of the fibre, as in cellulose acetate the hydroxyl groups is replaced by acetyl groups and also because of the greater regularity of structure. ~~While~~ Tricel fibres are more highly crystalline than ordinary acetate fibres. They absorb less water, because of the removal of all the hydrophilic hydroxyl groups and hence their properties would not be expected to vary much with increased humddity.

However it has been explained by Morton and Hearle,[80] that with non swelling medium, there is always an initial increase in density followed by a fall in density i.e. the density regain curve passes through a maximum which occurs at 3-12% moisture regain, depending on the type of the fibre. Thus it is reasonable to believe that the density decreases due to expansion and swelling of the fibre structure.

Effect of temperature

In every case with the exception of viscose rayon the density has decreased with an increase of temperature. A decrease in density would be expected if the volume of the fibre increased relative to the mass of the fibre. Inspection of the literature has shown that there has not been a great deal of work on this aspect but it has been explained by Morton and Hearle[80] that in most materials the behaviour on change of temperature is simple. As the temperature rises the material expands slightly, and when a certain temperature is reached it melts into a liquid. With fibres, the behaviour is more complex. As the temperature rises they may contract, instead of expanding. This contraction may be reversible, and when a critical temperature is reached it may become very pronounced. Fibres rarely show a sharp melting point, either they soften over a wide range of temperature or they may char or decompose before they melt. Other changes may occur at low temperatures.

Some references to the thermal expansion of textile materials have been found. Russell and Van Kerpel[52] quoted values of the expansion coefficient ($cm^3/gm/^oC \times 10^{-4}$) for secondary acetate as 1.84 between -30^oC and 54^oC and 2.45 between 54^oC and 115^oC

and for triacetate as 1.72 between -30°C and 40°C and 2.04 between 40°C and 120°C. According to these figures the density of secondary acetate should be affected to a greater extent with a rise in temperature than triacetate and the present results show that this has been the case.

Values of 1.6 and 3.7 $cm^3/gm/^oC \times 10^{-4}$ for the coefficient of volume expansion of Terylene in the ranges of -30°C to 60°C and 90°C to 190°C respectively, have been given by Mullins[81] while corresponding values for nylon 66 of 3.9 and 4.9 $cm^3/gm/^oC \times 10^{-4}$ below and above 49°C have been given by Boyer and Spencer.[91] The respective gradients of changes of density with temperature are in agreement with these values. The behaviour of viscose rayon has been found to differ from that of the other fibres with the density decreasing with an increase of temperature and then increasing with a further rise in temperature. No values for the volume expansion of viscose rayon were found but in one paper[92] dealing with the force - temperature behaviour of cellulose model filaments low linear expansion coefficients were quoted. Values increased with orientation but a negative value was recorded for an isotropic filament. It was suggested that the force temperature behaviour was not dependent on orientation alone but also on the

type of micro structure of the rayon with differences in swelling characteristics brought about by differences in the morphological structure of the fibre. A "glass transition" point for cellulose at 62°C has been reported,[93] and although no other mention of this has been found the present results could suggest a change in behaviour about this temperature. Alternatively the effect in the present instance could be a temporary one due to the presence of voids and it is suggested that the experiments might be repeated on viscose rayon which has been heated, cooled, and then tested at increasing temperatures. Mention should be made that a similar pattern of behaviour for viscose rayon to that shown above has been recorded by Juilfs.[53]

The effect of temperature on the density of polypropylene, polyethylene and polyurethanes was also measured at 0% r.h. with the temperature varying by steps over a range of 20°C - 70°C. The results have been shown in Tables 12 and 13. A cubical thermal expansion coefficient of 9.4 $cm^3/gm/^oC \times 10^{-4}$ below 81°C has been reported for polyethylene by Boyer and Spencer.[91] No corresponding value could be found for polypropylene but values of linear expansion[94] below another transition temperature (-122°C for polyethylene and -20°C for polypropylene) showed the rate of expansion of

TABLE 12

EFFECT OF TEMPERATURE ON DENSITIES OF POLYPROPYLENE AND POLYETHYLENE

TEMPERATURE	POLYPROPYLENE	POLYETHYLENE
°C	DENSITY g/cm^3	DENSITY g/cm^3
20	0.915	0.927
30	0.914	0.926
40	0.913	0.924
50	0.912	0.921
60	0.909	0.916
70	0.906	0.918

TABLE 13

EFFECT OF TEMPERATURE ON DENSITIES OF POLYURETHANE

TEMPERATURE	LYCRA DENSITY	CHEMSTRAND DENSITY	SPANZELLE DENSITY	GLOSPAN DENSITY	VYRENE DENSITY
°C	g/cm^3	g/cm^3	g/cm^3	g/cm^3	g/cm^3
20	1.153	1.216	1.265	1.275	1.322
30	1.146	1.210	1.261	1.270	1.315
40	1.139	1.205	1.256	1.264	1.308
50	1.134	1.198	1.249	1.259	1.302
60	1.128	1.191	1.244	1.253	1.296
70	1.123	1.187	1.238	1.248	1.289

polyethylene to be some 20% greater than that of polypropylene. The percentage change in density with temperature was calculated based on a dry fibre at 20°C, and the results have been shown in Fig.16 for polypropylene and polyethylene and Fig.17 for polyurethane.

These results, reveal some interesting points. First both polypropylene and polyethylene fibres give curved lines, and the curvature being such that apparent density gradually decreases at lower temperatures between 20 - 40°C, but thereafter rapidly decreases at higher temperatures, which makes the curvature more predominant, (Fig.16); Second all the polyurethane fibres give straight line graphs and the linearity being such that the apparent density decreases at lower temperatures and this becomes slightly more predominant at higher temperatures (Fig.17). The curve of polypropylene is less steep than polyethylene, indicating that the polypropylene is less affected than polyethylene with higher temperatures. Hahn et al[82] measured the volume coefficient expansion of polyethylene. The results were plotted as volume temperature. They found that the volume coefficient of expansion increased with temperature. Inspection of the results showed that

the general shape of the curve shows similar trends to those found in the present experiments, as shown in Fig.16. In general it is seen that the effect of temperature on the density of these fibres is considerable, and it would appear from these figures that slight variation in higher temperature will lead to a considerable variation in density. These observations bring about the importance of temperature control in density measurements.

Polypropylene is a most deformable fibre with temperature. Natta and Corradini[83] put forward a theory reasonably widely accepted, that on account of the methyl groups, a planar structure is impossible. Slinchter and Mandell[84] employed a proton magnetic resonance method, which was useful in establishing that the methyl groups were responsible for a low temperature transition believed to exist in polypropylene. To form a basis on which to interpret the results of the present investigation, the structural data of Monstead[85] are used. Chemically it would be assumed that polypropylene fibres are made from a polymer or copolymers of propylene. While polyethylene is a waxlike crystalline polymer which is flexible from its low temperature brittle point in the neighbourhood of 115°C Hunter and Oakes[86] observed that the density of

polyethylene at room temperature remained unchanged and then decreased gradually up to 50°C; thereafter it fell rapidly until the specimen was completely amorphous, at a temperature between 100°C and 120°C. They reported that the density of the molten polyethylene was slightly dependent upon average molecular weight and on the nature of the sample, but the temperature at which crystalline material first appears on cooling was raised by an increase in molecular weight. In the case of polyurethane intermolecular forces, sometimes called secondary chemical bonds, are the result of hydrogen bonding, dipolemoments and dispersion effect. These intermolecular attractive forces tend to hold polymer chains together in a manner similar to that of primary chemical bonds but are much weaker and are more readily affected by increase in temperature.

4. DENSITIES OF SOME POLYPROPYLENE FIBRES.

It was the purpose of the present investigation to determine whether any significant difference in the density values of the three types of polypropylene existed, and if so what could account for it. Hence the densities of polypropylene A, B and C were measured at a constant temperature 20°C, by the method explained previously. The results have been shown in Table 14.

TABLE 14

Densities of some dry polypropylene fibres.

Samples	Density g/cm^3	
	As received	Annealed
A	0.915	0.918
B	0.911	0.914
C	0.900	0.904

It is seen from these results that one effect of annealing was to increase the density of the fibre, but the order of ranking of the fibres remains the same suggesting that while exposure to a higher temperature may have caused increased crystallinity the rate effect on the three fibres has remained constant despite the differences in original density.

All the above observations are highly significant in terms of the fibre structure. They may be the result of a difference in the manufacturing process. Chemically it would be assumed that all these fibres have the same constitution, i.e. fibres made from polymer or copolymer of propylene, having the general formula $CH_2=CH.\ CH_3$.

In the past various theories (micelle theory, fringed micelle theory, continuous structure theory)

have been proposed regarding the molecular structure of the fibres. However none of these is self contained to explain all the varied phenomenon observed in polymers.

Wijga[37] reported that the degree of crystallinity, crystalline structure, average molecular weight, and molecular weight distribution are the variables mainly responsible for such properties, in which small deformations are involved; such as modulus of elasticity, softening point, and hardness, because its value is of great significance in connection with high temperature properties. He further stated, that in polyethylene the degree of crystallinity depends on the deviation, from linearity or regularity, of the long chain hydrocarbon molecules. The chain branching was held to be responsible for the decrease in crystallinity, but it was possible that the presence of double bonds and the presence of oxygen groups may have similar effect. Besides the overall degree of crystallinity a factor of importance for the mechanical properties of crystalline polymer is the way in which crystallisation has occurred. The average degree of crystallinity also affects the density value.

On the other hand, it is believed that if the copolymer is allowed to stand for a time prior to

spinning, it settles down more uniformly, and as a result of settling down, it is possible that it may assume a higher degree of crystallinity, which in turn may lead to a higher value of density. Samples A and B (Table 14) were in fact fibres or staple polypropylene whereas sample C was a filament, and the results were surprising in that increased crystallinity and orientation is normally expected in a filament as opposed to the fibre form of a material. Unpublished work suggests that filament C had a lower modulus and a higher breaking extension than fibres A and B, and if this were so it would confirm the density results and suggest that difference in density is due to differences in molecular spacing despite the form of the material. A decrease in the hydrogen bond spacing in polypropylene as a result of annealing has been reported by Dadami et al[88] and this would lead to an increase in crystallinity and a higher density as reported above. The results are also in keeping with those of Shibukawa et al[95] who have in addition done work on the temperature dependence of polypropylene and other fibres which again serves as confirmation of some of the work reported in this thesis.

5. EFFECT OF RESIN ON THE DENSITY OF VISCOSE RAYON

The effect of resin on the density of dry viscose rayon at 20°C, has been measured according to the procedure previously explained for other fibres. The results have been shown in Table 15.

TABLE 15

Effect of resin on density of dry viscose rayon

Resin used	Nominal concentration (%)	Density g/cm^3
Untreated	0	1.523
Melamine formaldehyde	7.2	1.514
Melamine formaldehyde	9.5	1.511
Ethylene urea formaldehyde	10.5	1.509
Ethylene urea formaldehyde	14.7	1.506
Methylated urea formaldehyde	11.0	1.517
Methylated urea formaldehyde	15.5	1.514
Urea formaldehyde	13.5	1.519
Urea formaldehyde	16.5	1.514

It is seen from these results that the density value of viscose rayon decreases with the resin treatment and in fact it appeared to vary linearly with the amount and type of resin present in the fibre. Azuma et al[96] determined the density of viscose rayon by using a displacement method. They found that the density of viscose rayon decreased with urea-formaldehyde resin treatment, and reported that the density of the resin treated fibres depended on the length of time in which they were allowed to stand in the precondensate solution.

Steele and Schiwall[97] measured the density of viscose rayon using the density gradient column method and stated that the density decreased with the amount and type of resin used. They further stated that the predominant effect was due to fibre swelling with very little resin being deposited in void spaces not previously accessible to the solvent mixture in gradient column.

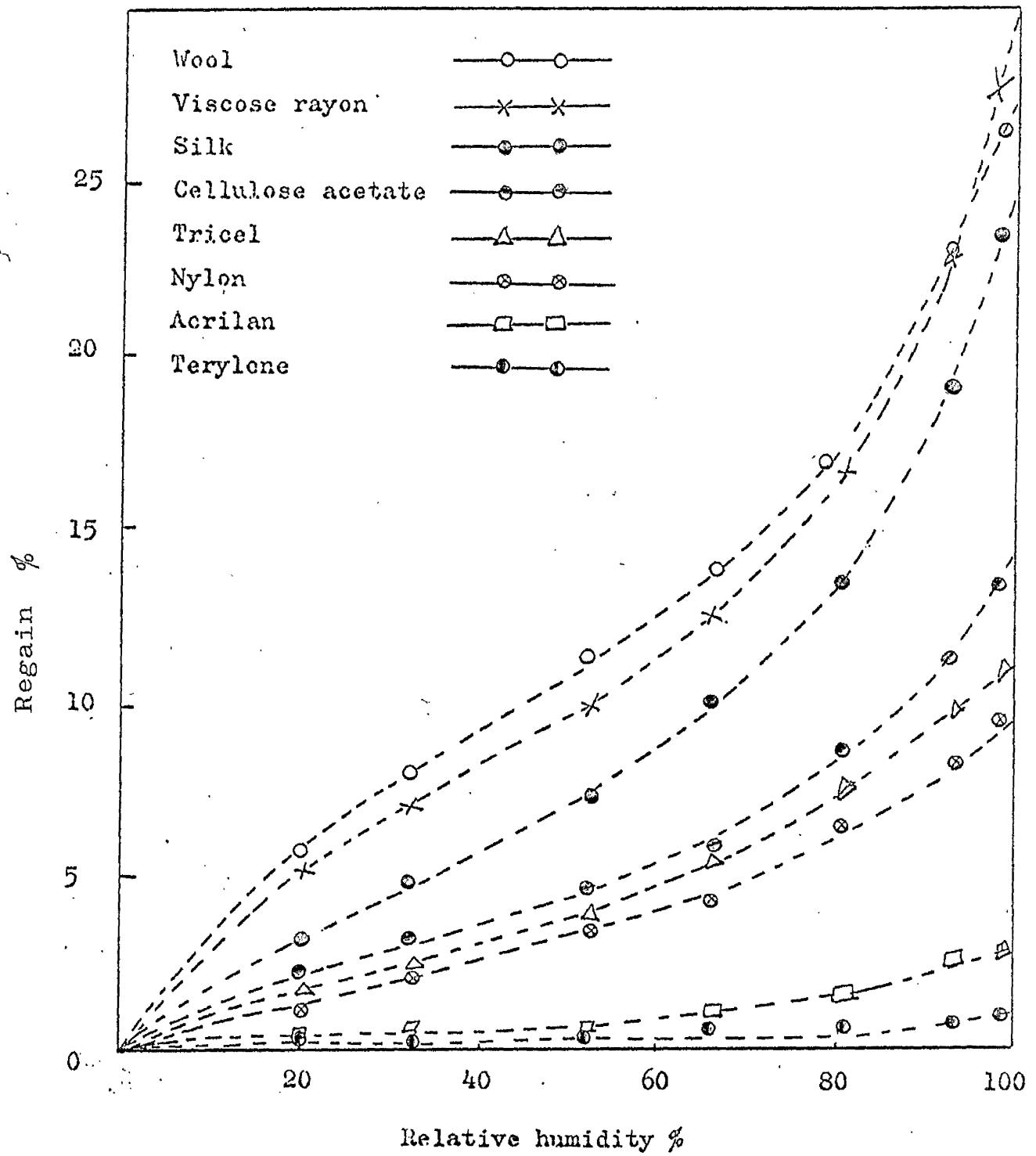

Fig.1. Sorption isotherms for textile fibres.

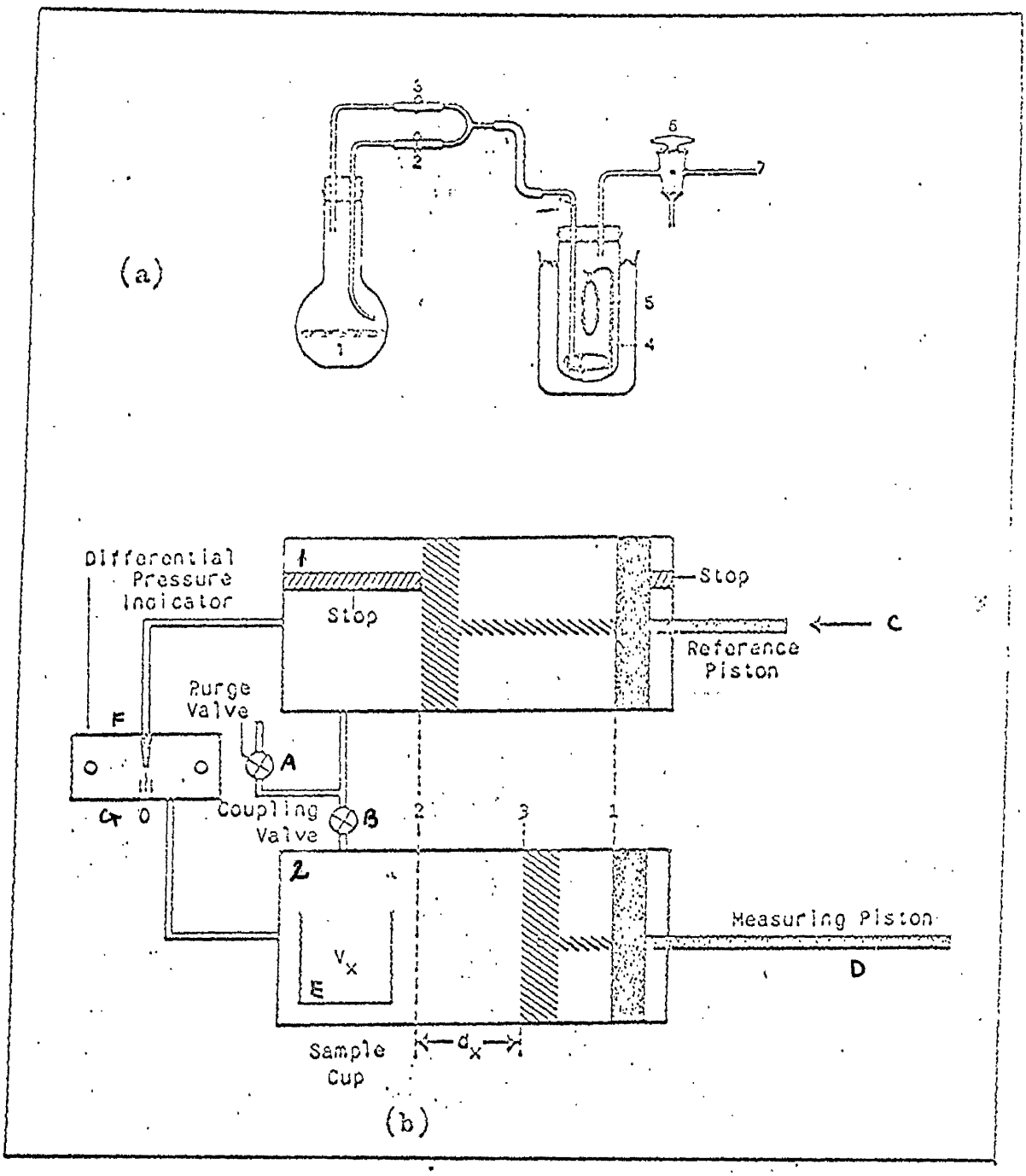

Fig 2(a) Apparatus used for driving out air from fibre material

Fig 2(b) Simplified schematic diagram of Beckman method

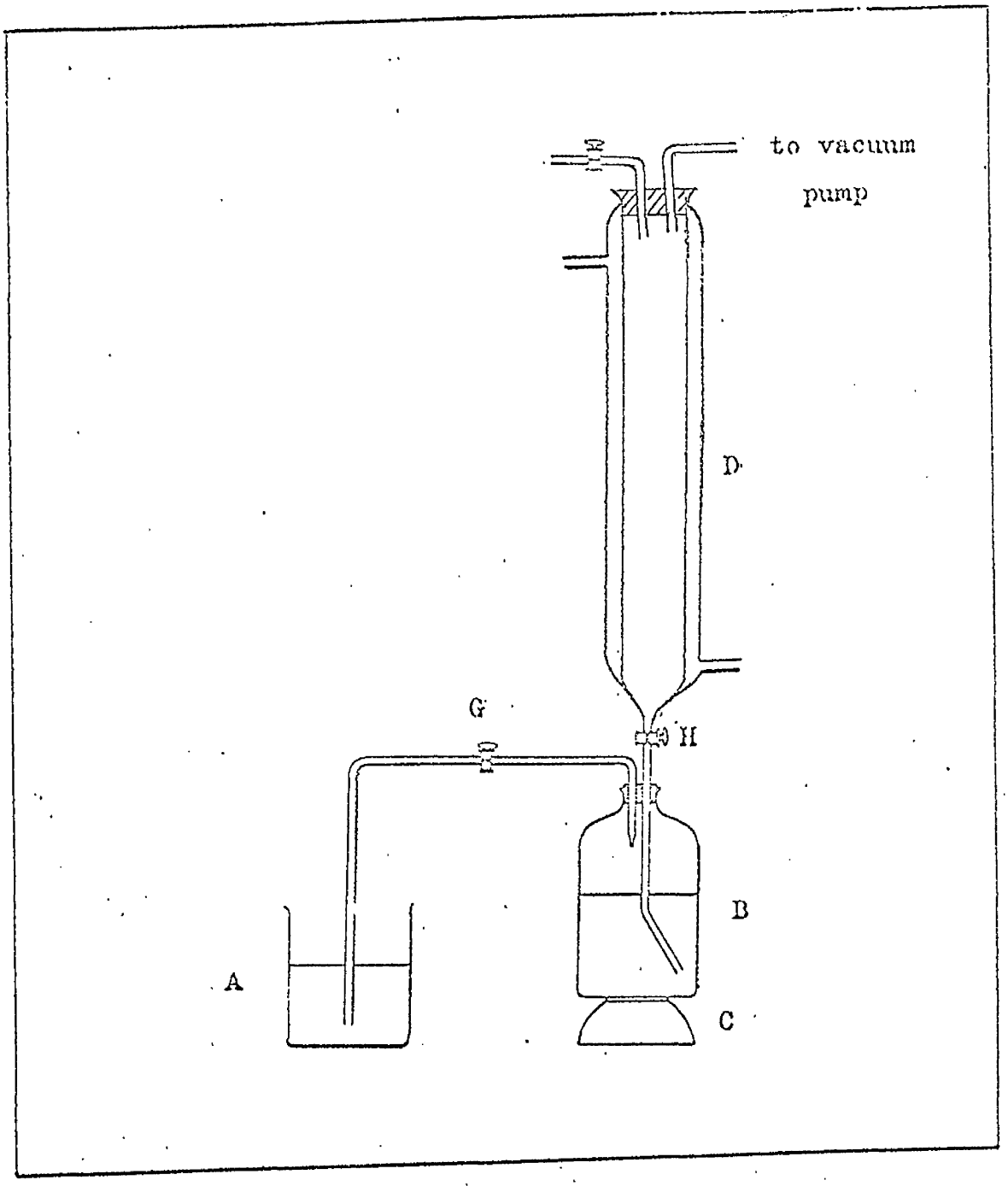

Fig. 3. Apparatus used for setting up a liquid column graded in density.

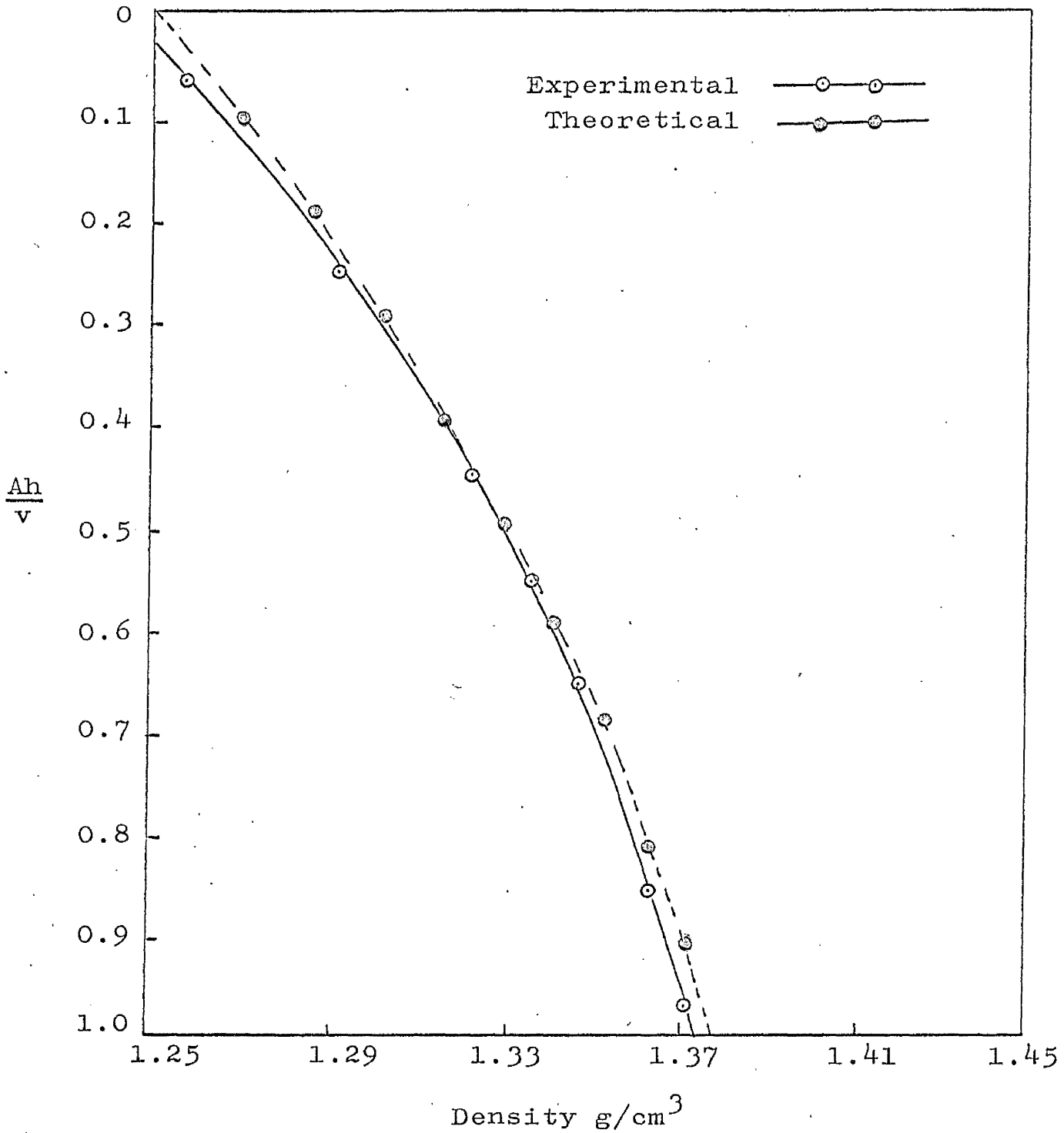

Fig.4. Typical density profile in a liquid column formed from a mixture of xylene and carbon tetrachloride.

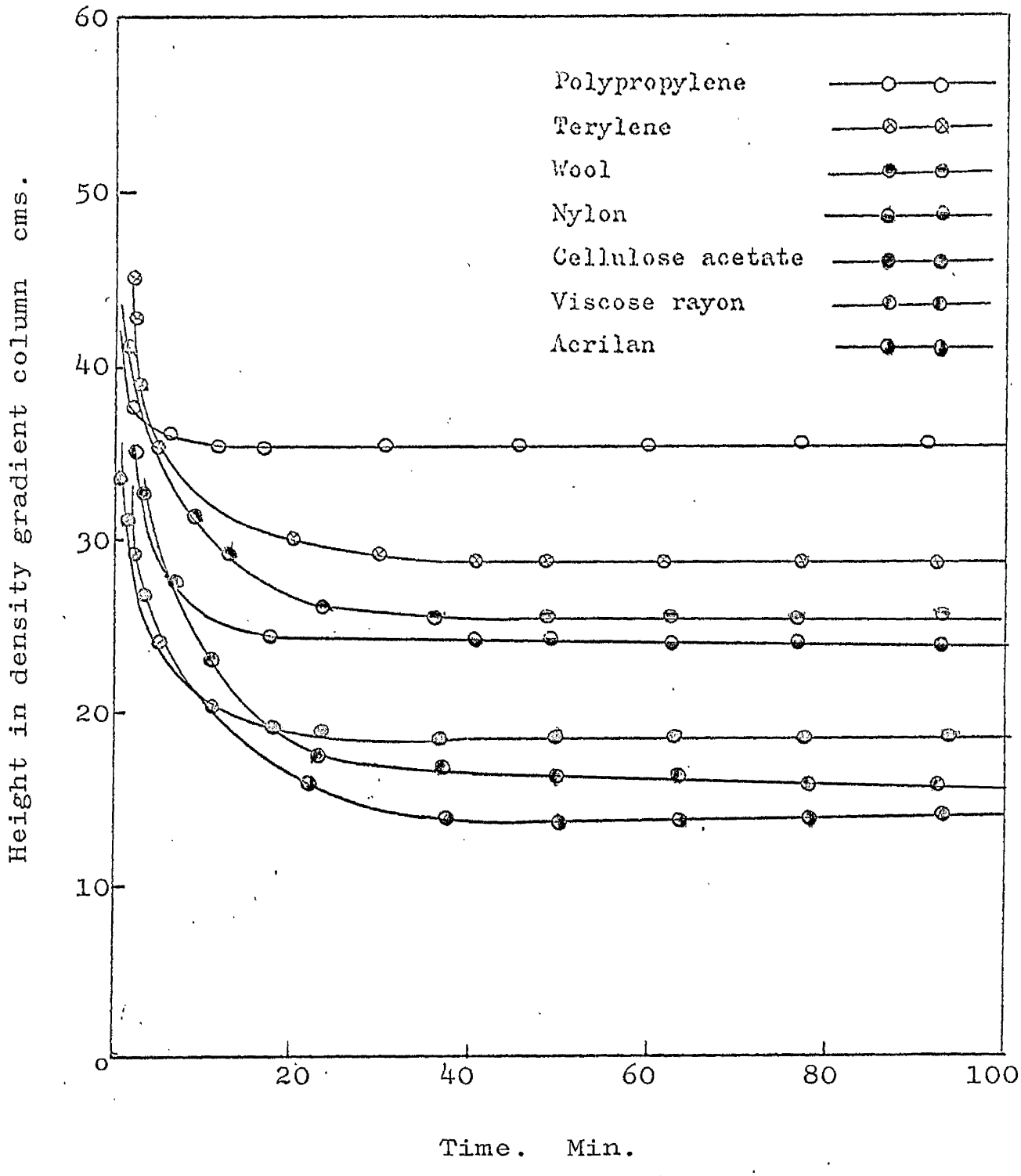

Fig.5. Equilibrium time of fibres in gradient column

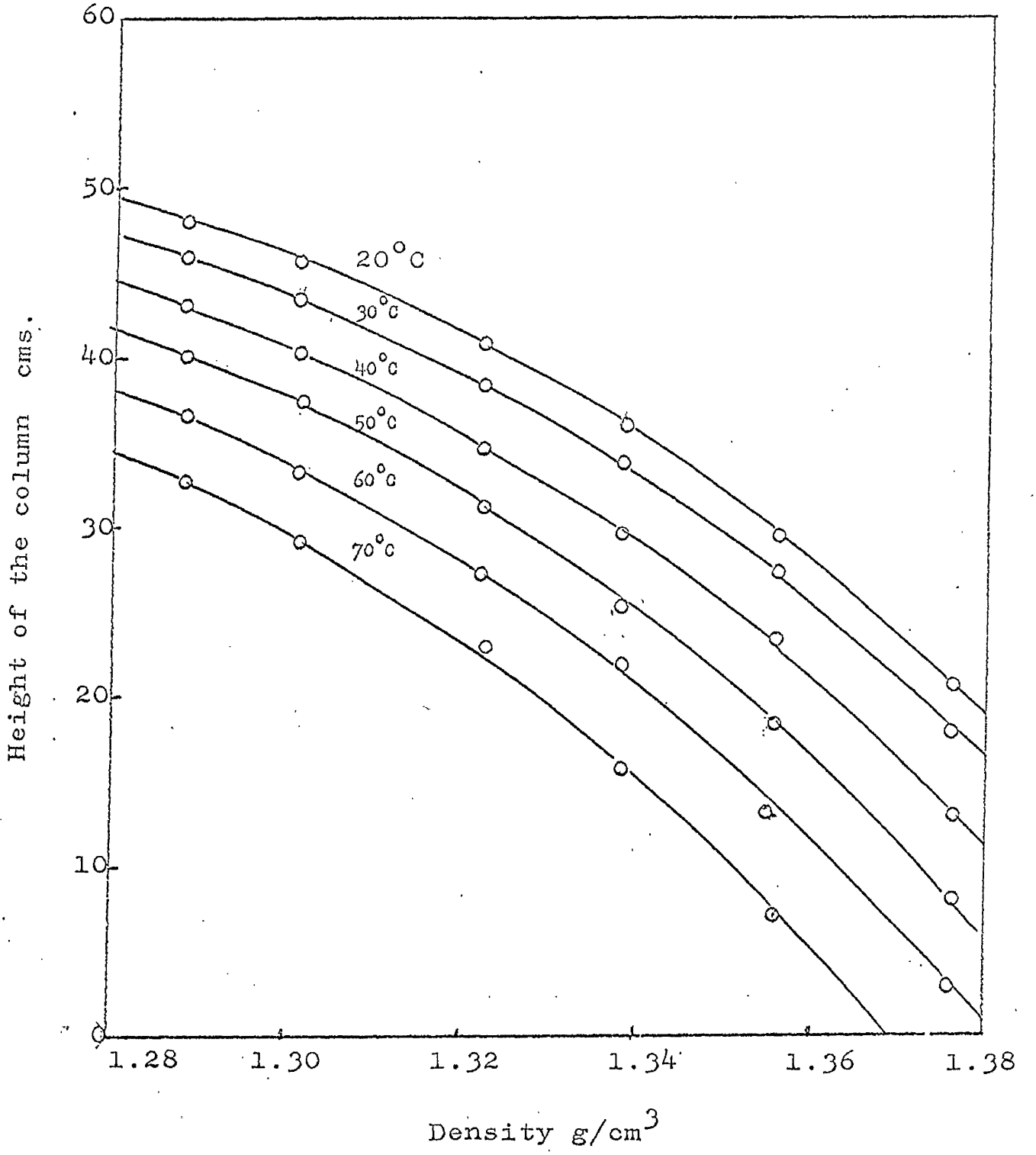

Fig.6. Effect of temperature on the density profile of a gradient column formed from a mixture of xylene and carbon tetrachloride.

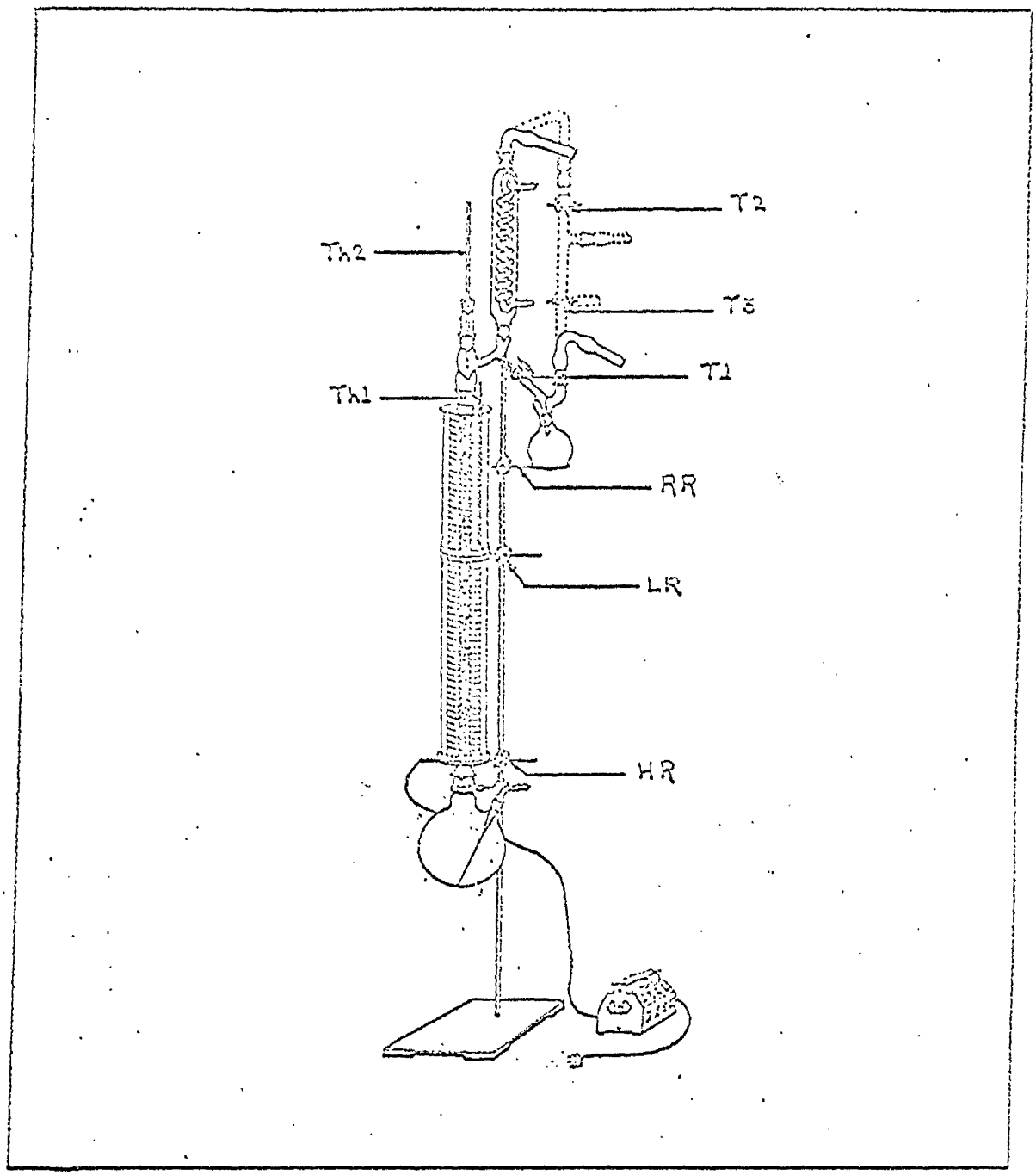

Fig. 7.

Fractional distillation unit.

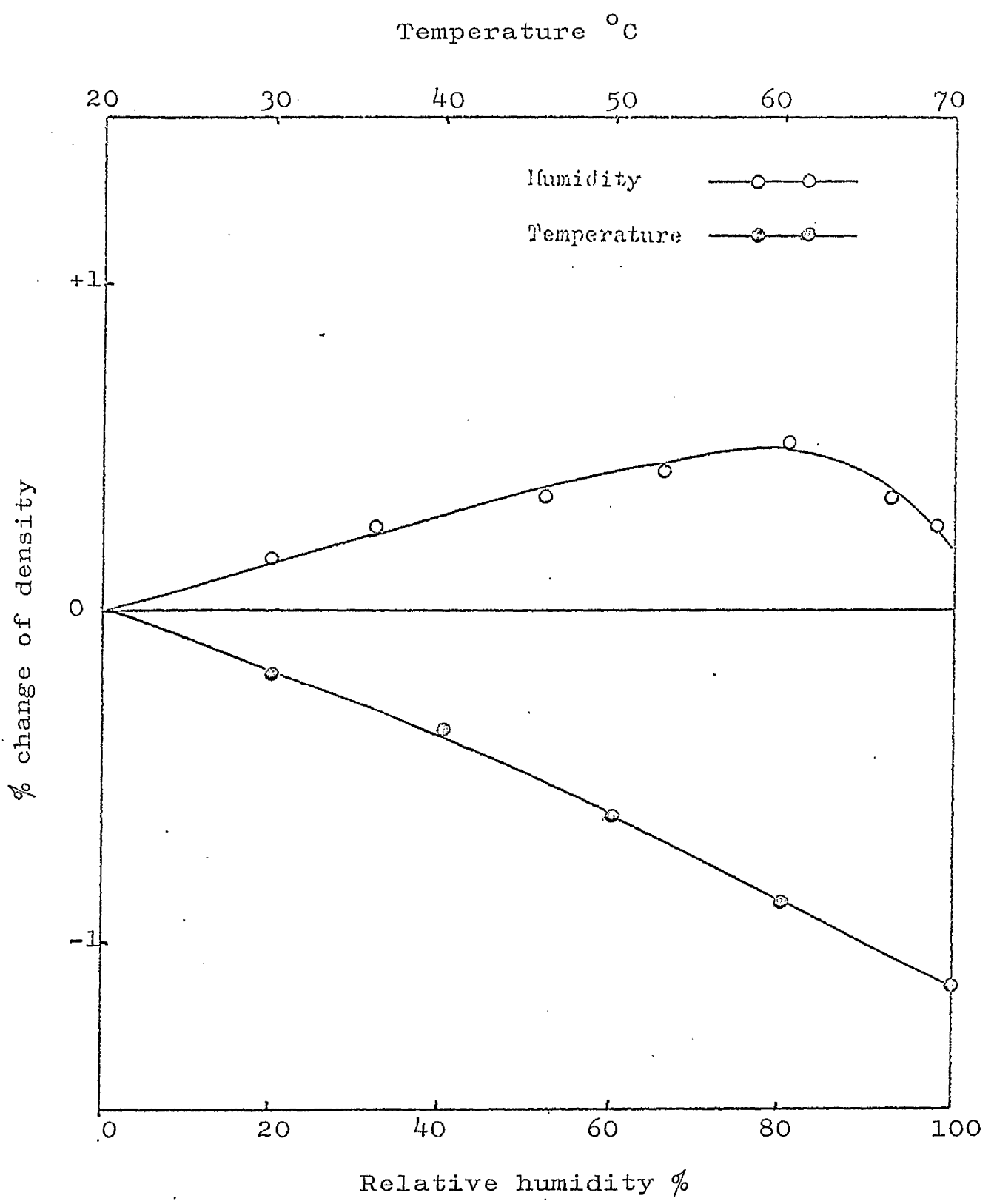

Fig.8. % change of density of nylon with temperature and humidity

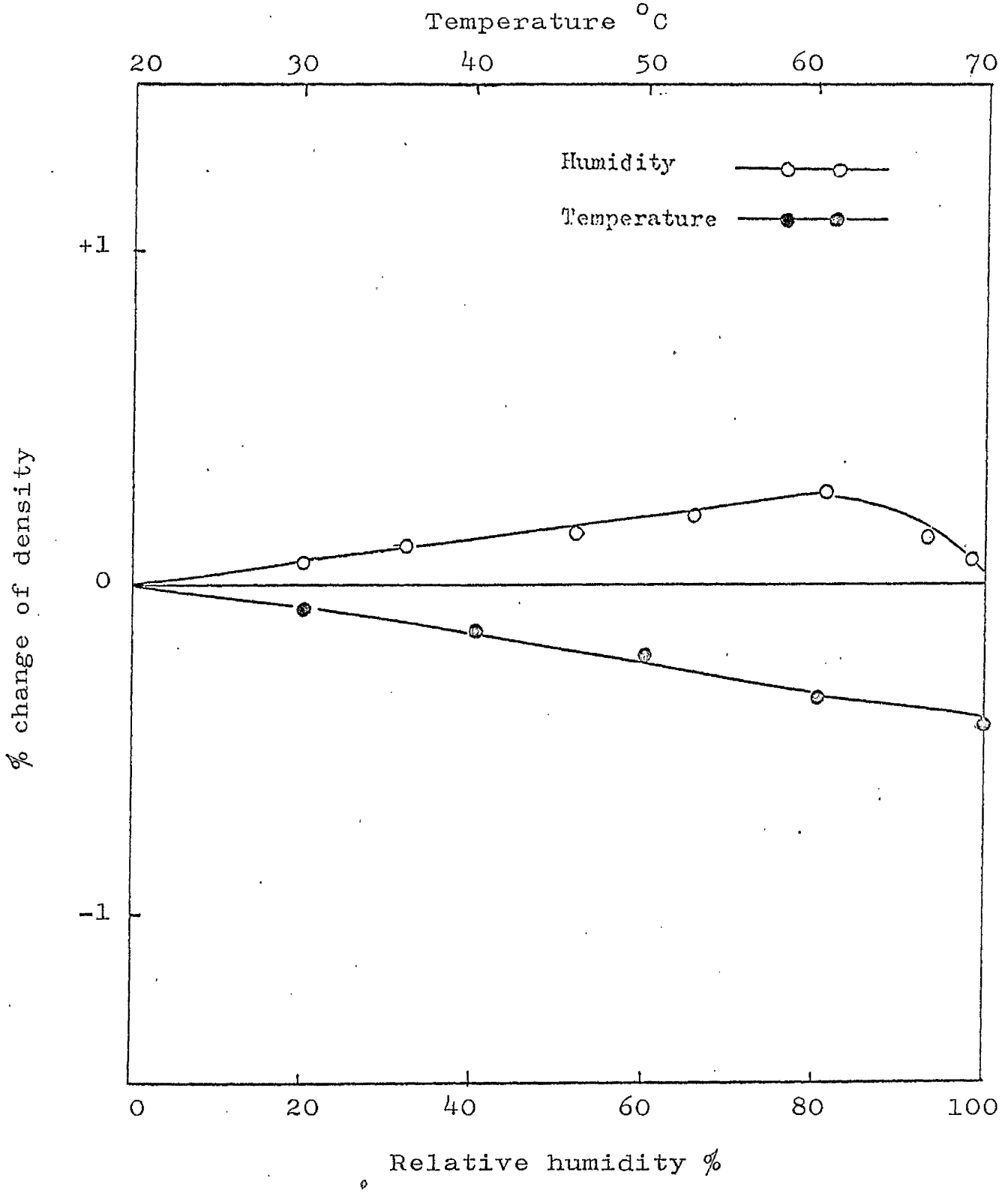

Fig.9. % change of density of Terylene with temperature and humidity

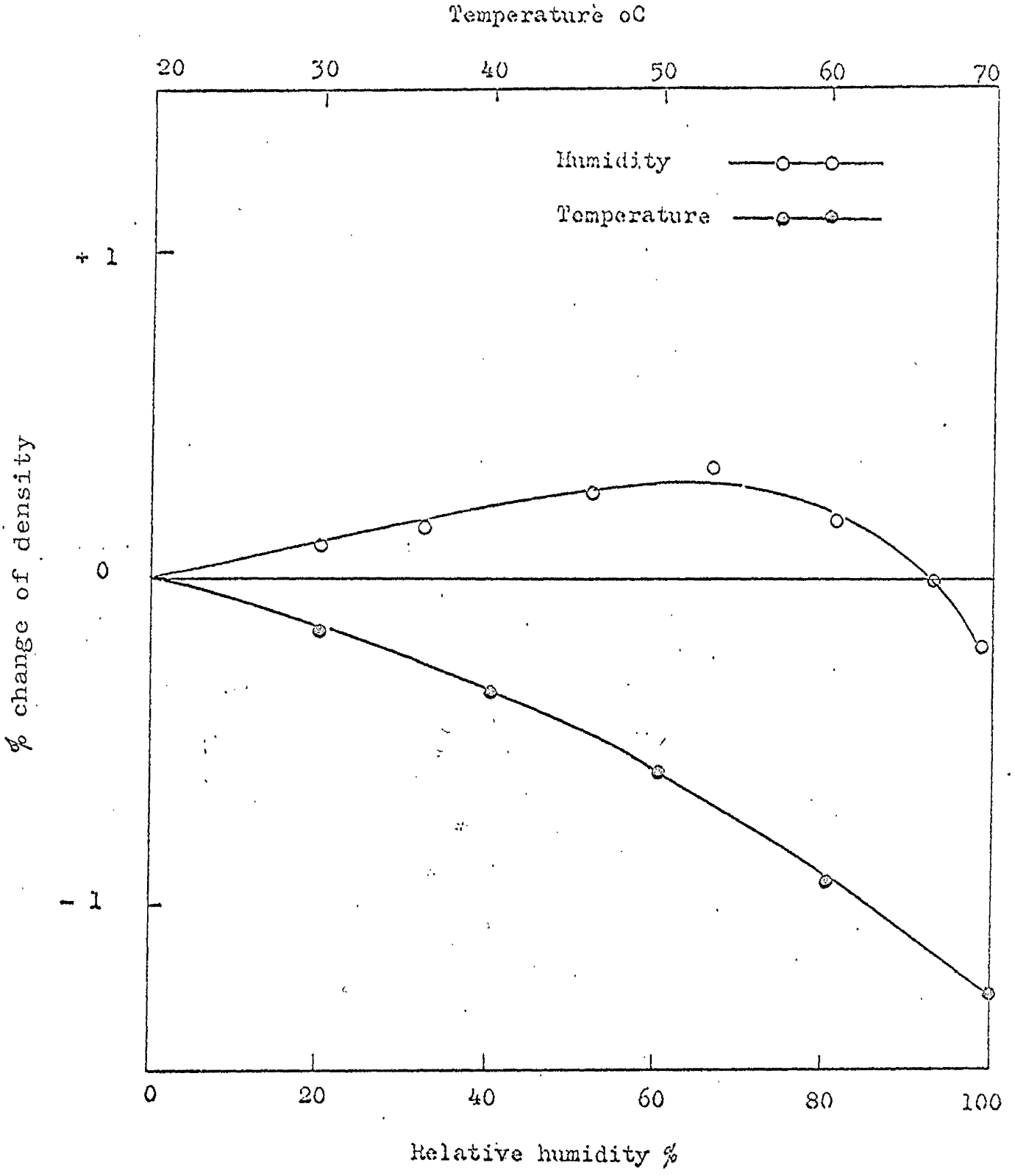

Fig.10. % Change of density of Acrilan with temperature and humidity.

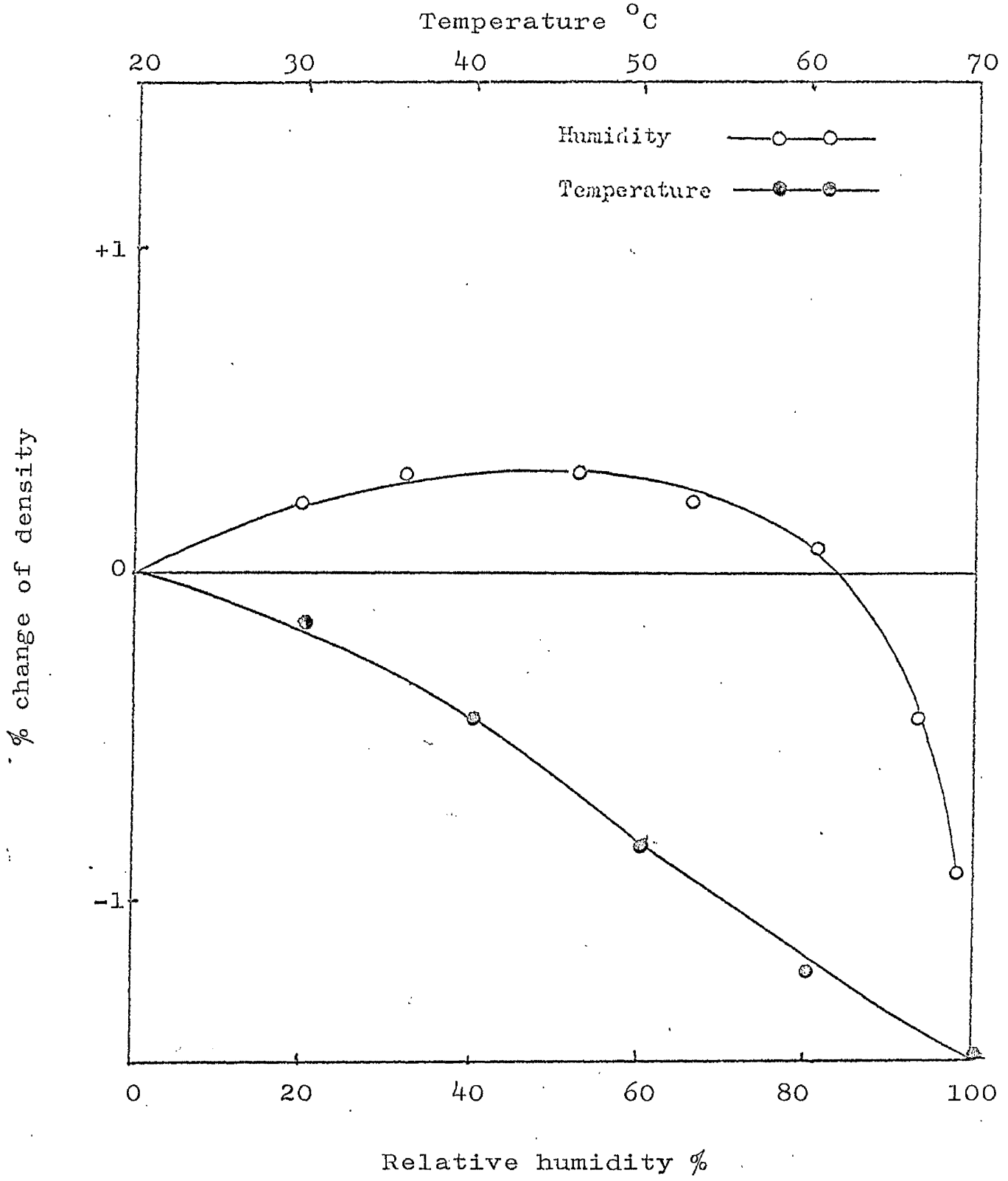

Fig.11. % change of density of wool with temperature and humidity

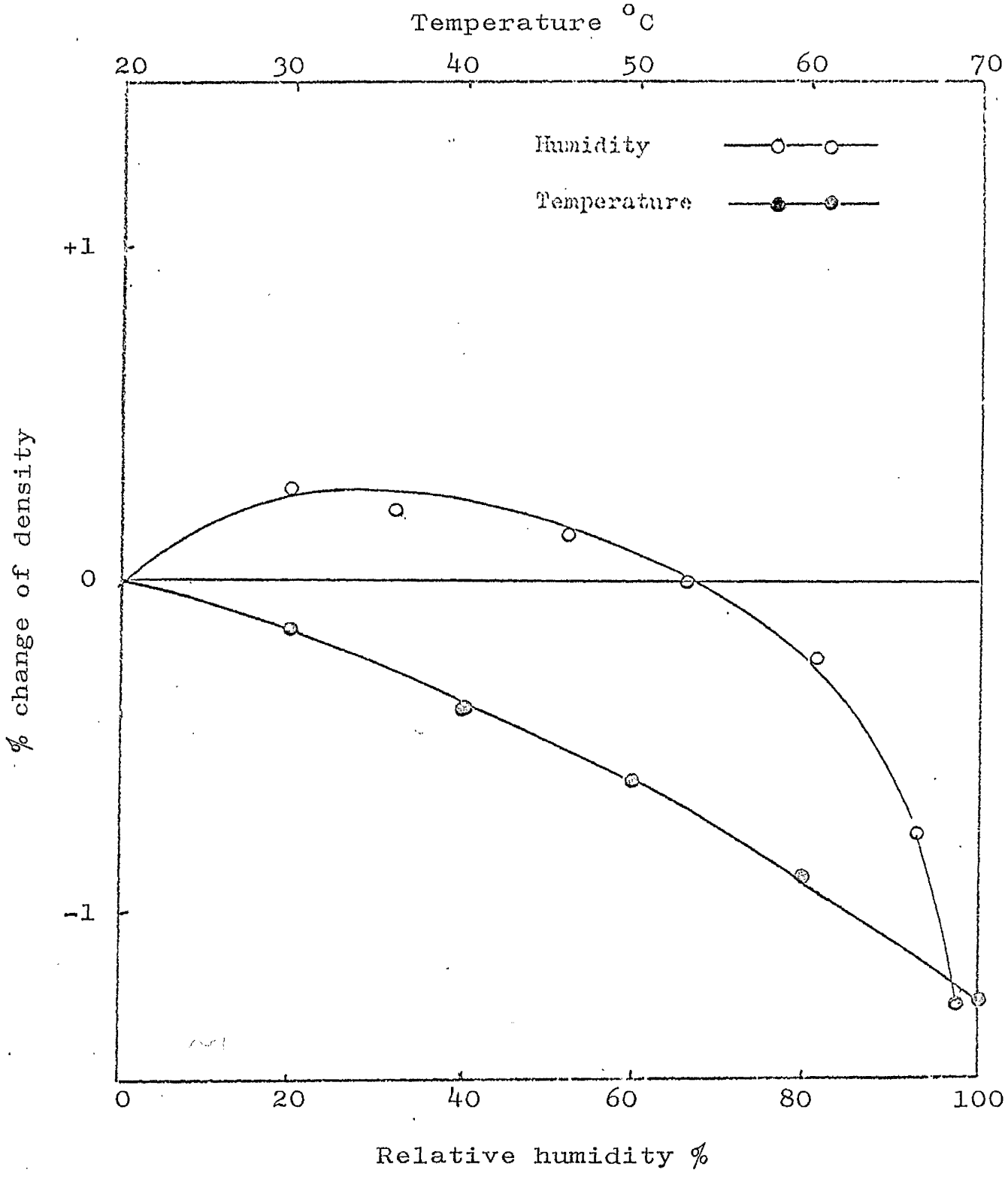

Fig.12. % change of density of silk with temperature and humidity

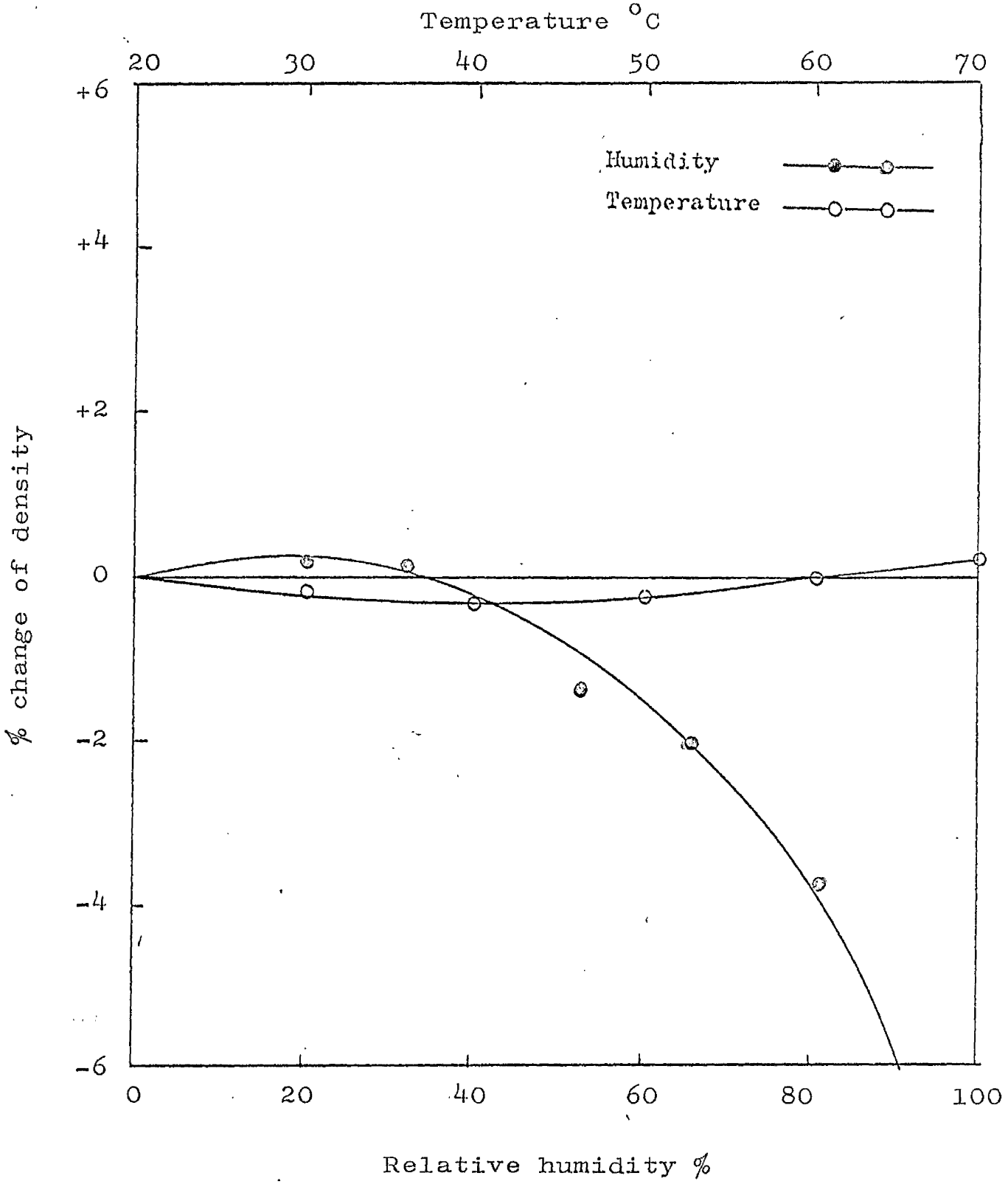

Fig.13. % change of density of viscose with temperature and humidity

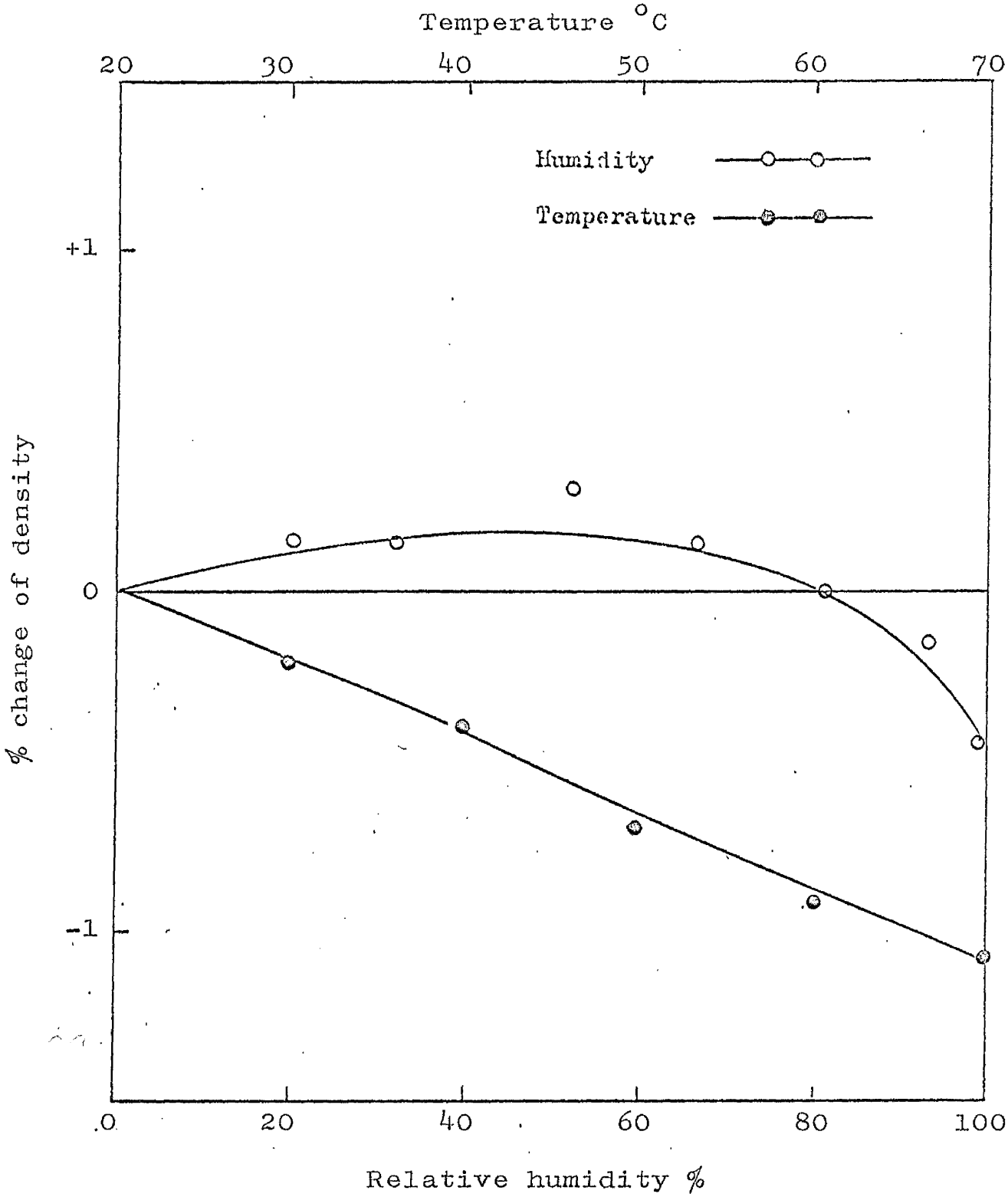

Fig.14. % change of density of cellulose acetate with temperature and humidity.

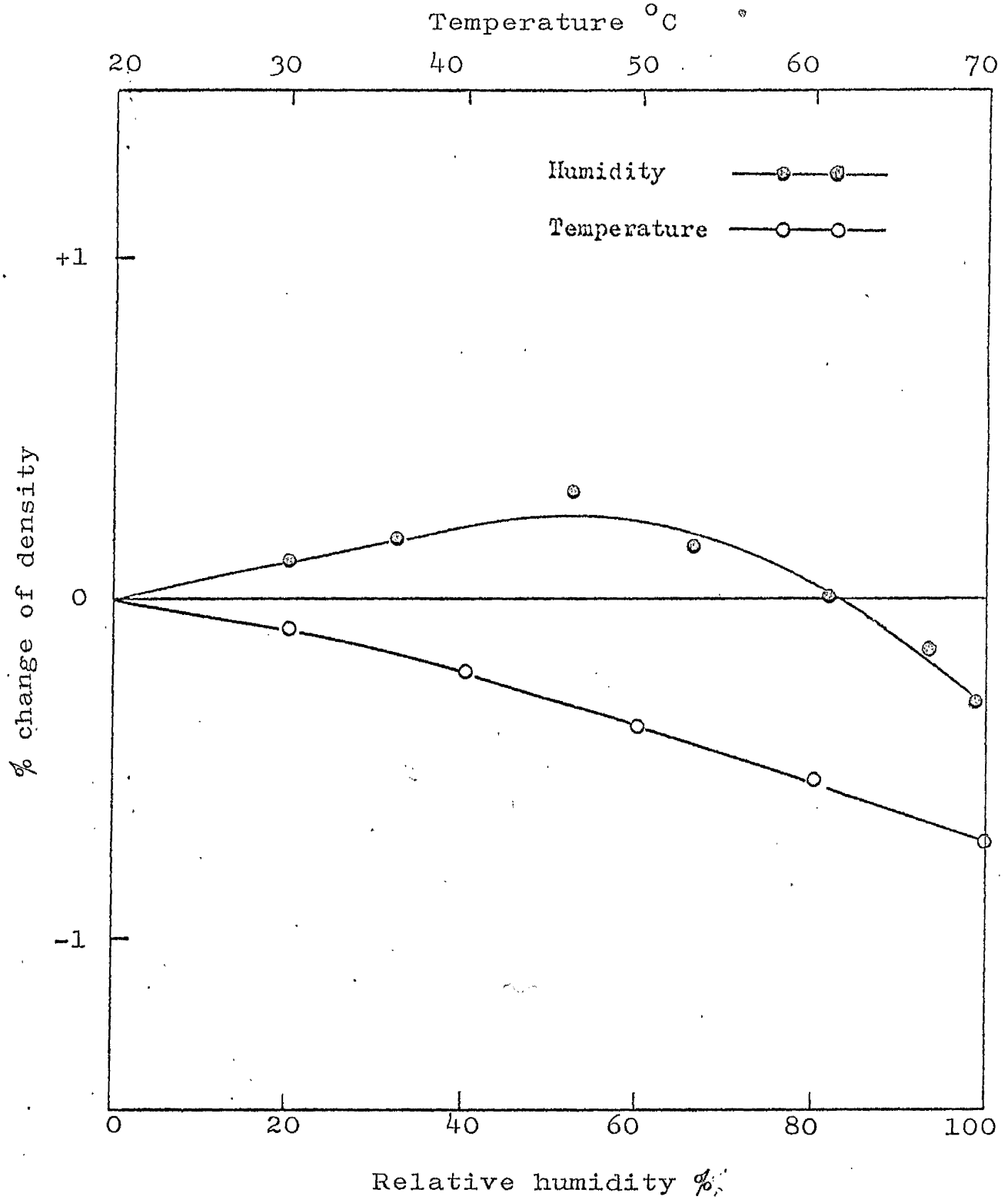

Fig.15. % change of density of Tricel with temperature and humidity

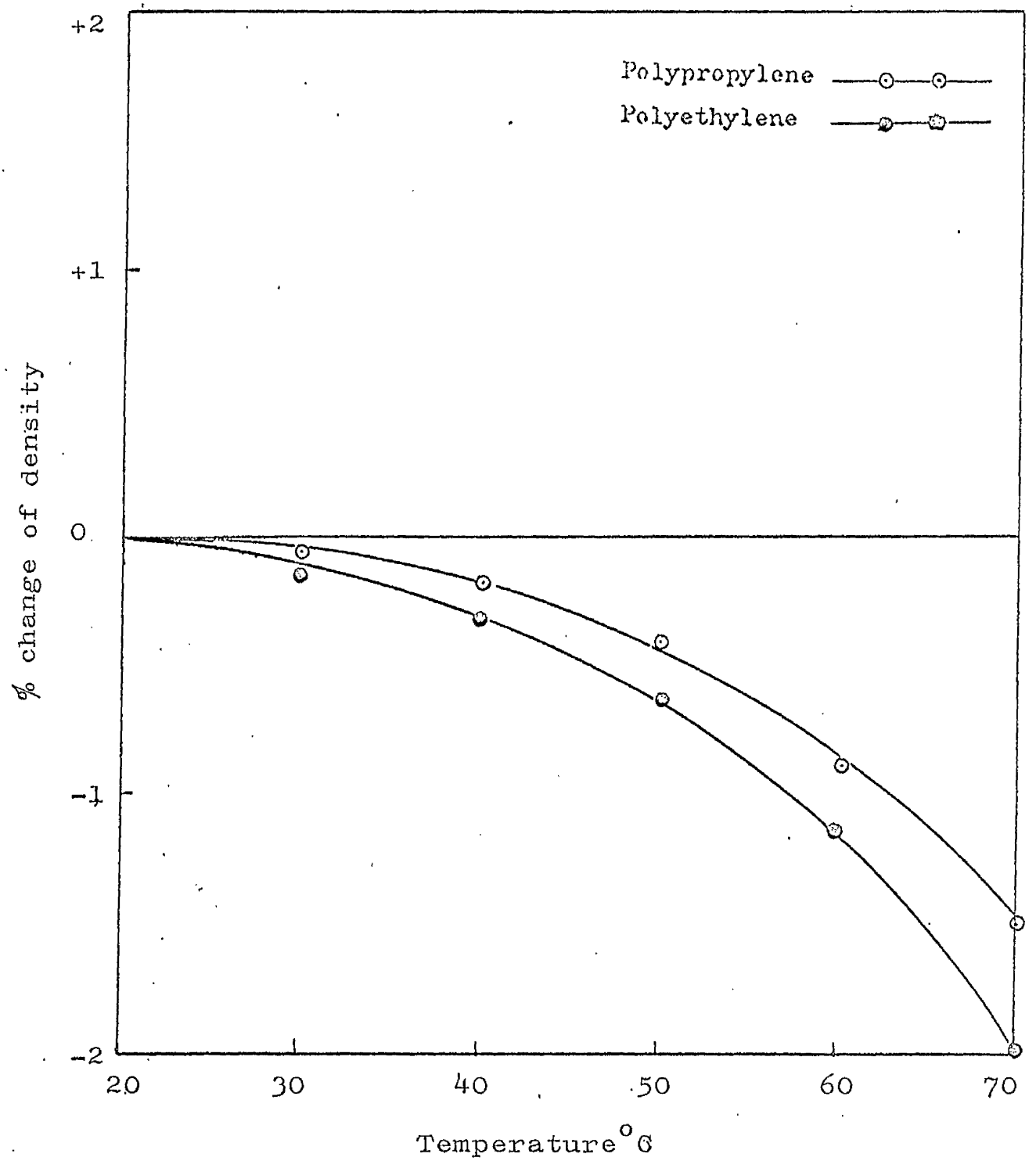

Fig.16. % change of density of polypropylene and polyethylene with temperature.

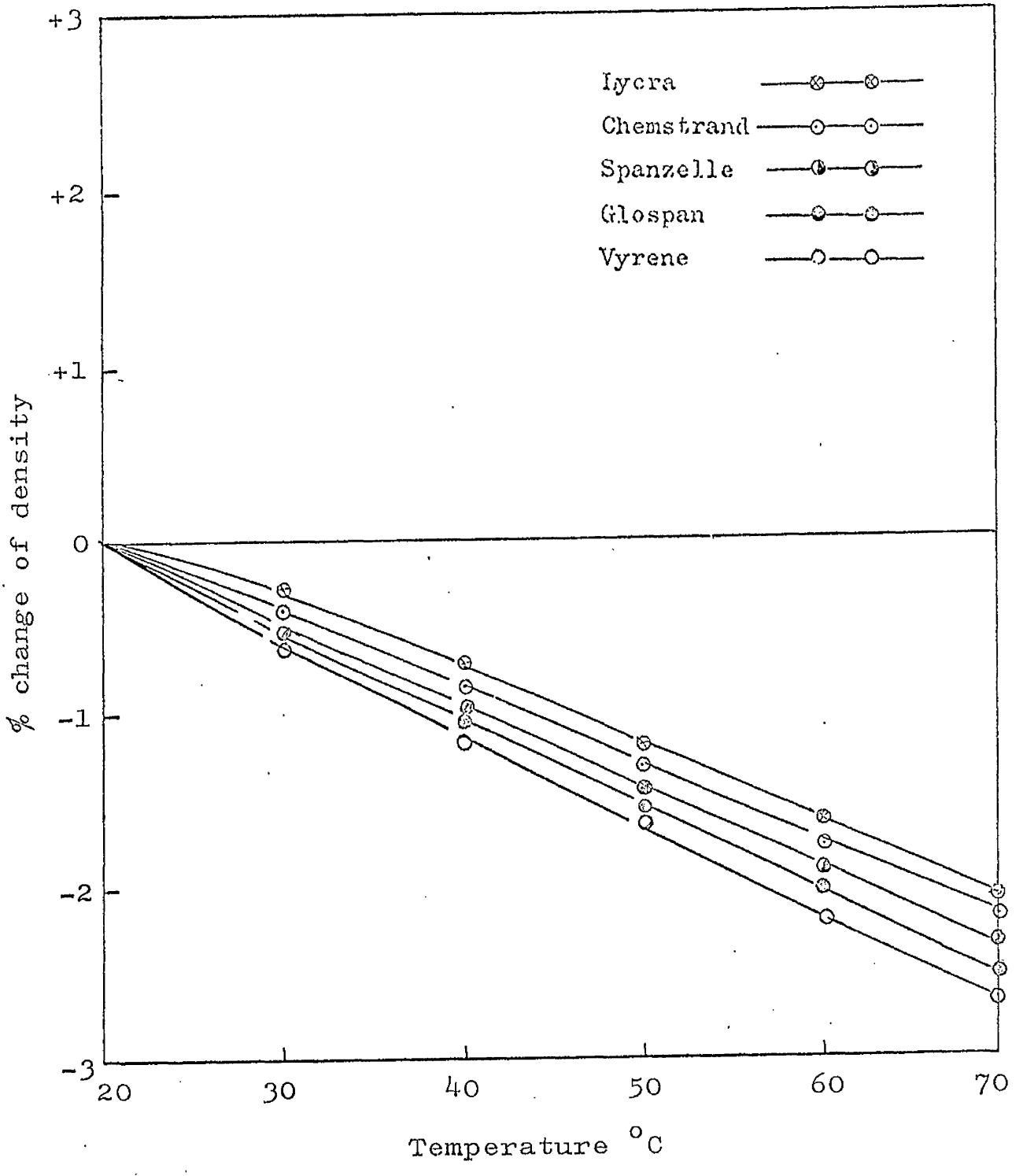

Fig.17. % change of density of polyurethane with temperature

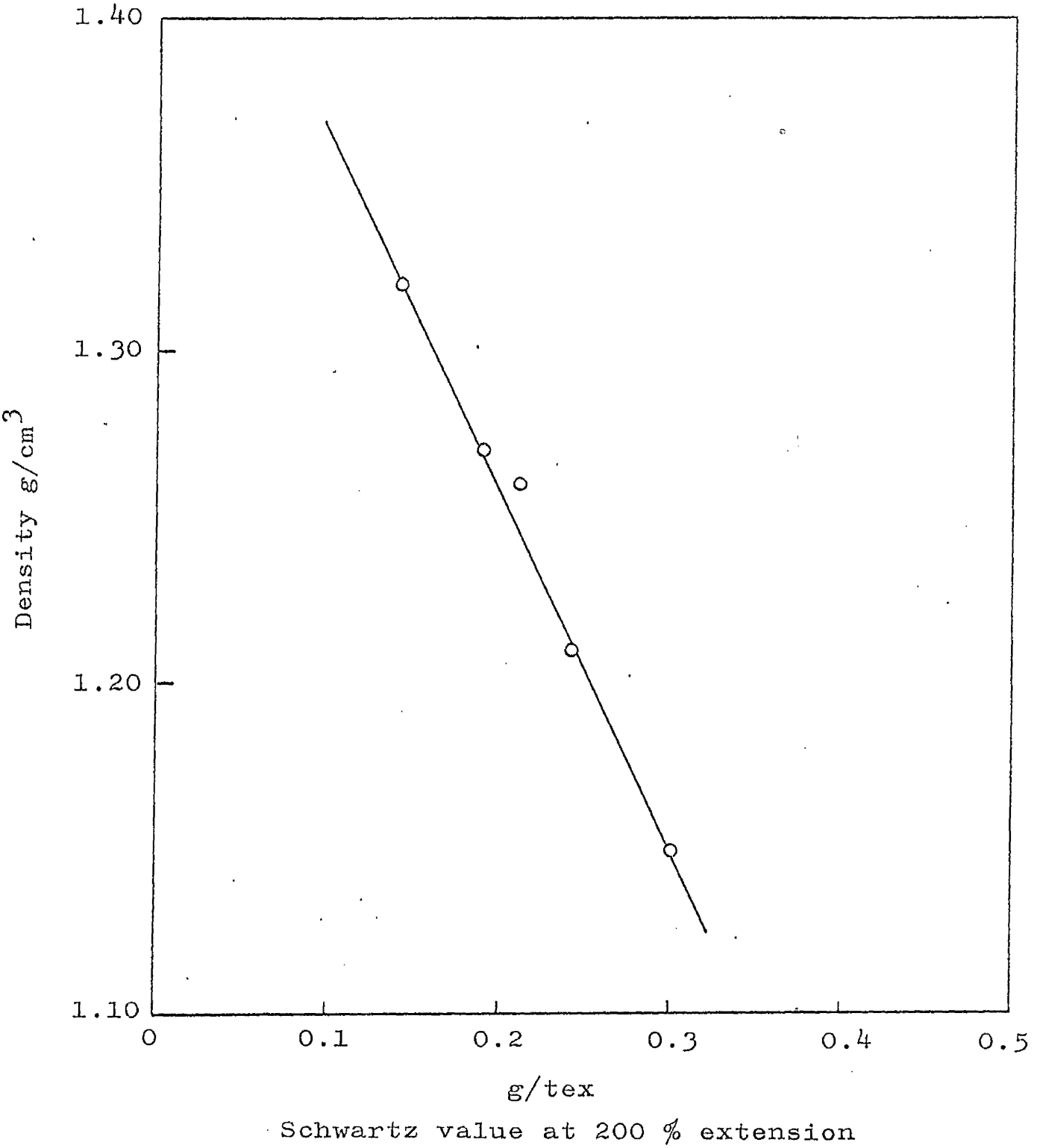

Fig.18. Relationship between Polyurethane fibre density and yarn Schwartz value at 200% extension.

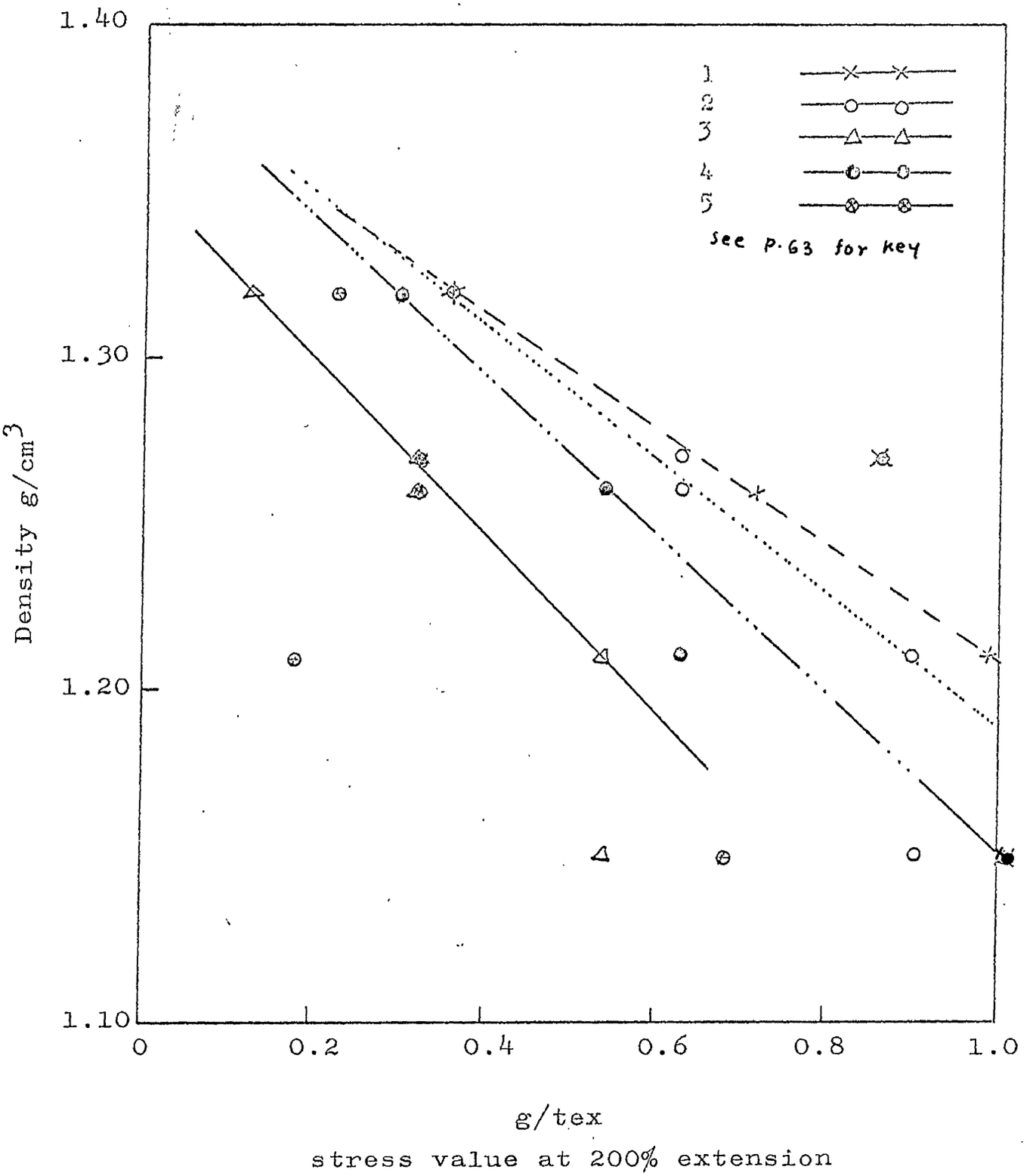

Fig.19. Comparison between Polyurethane fibre density and yarn stress at 200% extension..

REFERENCES

1	HERMANS, P.H., AND HERMANS, J.J.	J. Polymer.Sct., **1**, 149, 1946
2	COATES, E.D.,	J. Sct. Inst., **37**, 148, 1960
3	KING, A.T.,	J. Text. Inst., **17**, T.35, 1926.
4	SPEAKMAN, J.B.,	Proc. Roy. Soc., **A.132**, 167 1931.
5	DAVIDSON, G.F.,	J. Text. Inst., **18**, T.175, 1927
6	MELTZER, W.,	Chemische Und Physikalische Technologie, Der Kunstseiden., Berlin, 1929.
7	FILBY, F., AND MASS, O.,	Canad. J. of Research., **7**, 162, 1932.
8	LAUER, K., AND WESTERMAN, U.	Kolloid. Z., **107**, 69, 1944.
9	HERTJES, P.M.,	Rec. Trav. Chem., **61**, 751, 1942.
10	SHAW, A.J., AND HANSEN, L.A.,	J.Phys.Chem., **41**, 1007, 1937.
11	HERMANS, P.H.,	J. Text. Inst., **38**, P.63, 1947.
12	MULLER, F.H.,	Kolloid. Z., **100**, 355, 1942.
13	HAKIMI, H.,	Text. Res. J., **19**, 595, 1949.
14	ELOD, E., AND FROHLICH, H.G.,	Ibid., **16**, 452, 1946.
15	ABBOTT, N.J., AND GOODINGS, A.C.,	J.Text.Inst., **40**, T.232, 1949.
16	CAMPBELL, J.D., AND RUSSELL, J.K.,	Quart. Rev. Forest. Prod. Lab. Canada., **21**, 24, 1955.
17	ILLINGWORTH, J.V.,	Text. Recorder, **61**, 60, 1944.
18	FORTES, F.,	Text. Res. J. **19**, 23, 1949.
19	GAINES, G.L. AND RUTKOWSKI, C.P.,	Rev.Sct.Inst., **29**, 600, 1958.

20 HERMANS, P.H., HERMANS, J.J., VERMAAS, D., AND WEIDINGER, A. Rec.trav.chim., 63, 44, 1944.

21 HOLL, V., Bothefte.Zu.Bte Chemie., 42, 105, 1943.

22 HERMANS. P.H., Contribution to the Physics of Cellulose Fibres, Elsevier, Amsterdam, 1946.

23 SHABKOV, V.I., AND LEVANOVA, V.P., Zhur. Priklad. Khim. 32, 2557, 1959.

24 CRAIG, J.P., KNUDSEN, J.P. AND HOLLAND, V.F., Text.Res.J, 32, 435, 1962.

25 TAKAHASHI, K., AND NUKUSHINA, Y., J. Polymer.Sci., 56, S.19, 1962.

26 ROCHAS, P., Bull.Inst.Text.France., 71, 95, 1957.

27 HIRIENT, F., AND PEPPER, E.L., Densities of Solid and Liquids, natural, Bureau. of standard circular., 487. 1950.

28 ANDERSON, N.G., AND ANDERSON, M.L., Anat. Record., 120, 709, 1954.

29 DOCK, E.M., AND MANSING, L., Anat. Chem. 26, 1543, 1954.

30 FORTUIN, J.M.H., J.Polymer.sci., 44, 505. 1960.

31 MILES, J.M., Ibid., 19, 535, 1956.

32 LINDSLEY, C.H., Text.Res.J., 22, 237, 1956.

33 ANDERSON, N.G., Science, 121, 775, 1955.

34 LINDERSTRØM-LANG, K., Nature., 159, 713, 1939.

35 LINDERSTRØM-LANG, K., AND HENRY LANE., Jr.Microchim. Acta, 3, 210, 1939.

36 LINDERSTRØM-LANG, K., JACOBSEN, O., AND JOHANSEN, G., Compt.Rend.trav.Lab.Carlsberg. Ser'.chim. 23, 17, 1939.

37 DOYER, E.F., SPENCER, R.S., AND WILEY, B.M., J.Polymer.sci. 1, 299, 1946.

38	ANDERSON, N.G.,	Rev.sci'.Inst., 26, 891, 1955.
39	TUNG, L.H., AND TAYOR, W.C.,	J.Polymer.sci. 17, 441, 1955.
40	TESSLER, S., WOODBERRY, N.T., AND MARK, H.,	Ibid., 1, 457, 1946.
41	METLAUFER, D.B.,	Nature, 180, 1122, 1957.
42	PRESTON, J.M., AND NIKKAV, M.V.,	J.Text.Inst. 41, T.446, 1950.
43	STOCK, C.R., AND SCOFIELD, E.R.,	Text. Res. J., 21, 821, 1951.
44	MIKHAILOV, N.V., FAINBERG, E.Z., AND KOHLER, M.,	Vysokomol.soed. 2, 1051, 1960.
45	STEFANI, R.M., CHEVRETON, M., GARNIER AND LYRAUD, C.,	Comp.Rend. 251, 2174, 1960.
46	KENNEDY, J.P., AND FONTANA, C.M.,	J.Polymer.sci., 39, 501, 1959.
47	KOYANO, K., AND NAGO.,	Kolloid.Z., 177, 30, 1961.
48	ROSENBAUM, S.,	J.App.Polymer.sci., 7, 1825, 1963.
49	HURLEY, R.B., AND TENTIS, L.S.,	J.Polymer.sci., B.1, 425, 1963.
50	RIPA, O., AND SCHNEIDER, W.C.,	Text.Res.J. 32, 455, 1962.
51	AUSTIN, J.C., AND ROBERT, J.J.,	Ibid., 26, 305, 1956.
52	RUSSELL, J., AND VAN KERPEL, R.G.,	J.Polymer.sci., 25, 77, 1957.
53	JULES, J.,	Holland Textiber 40, 963, 1959.
54	STAMM, A.J., AND SEBORG, M.,	J.Phys.chem., 39, 135, 1935.
55	SPEAKMAN, J.B., AND SAVILLE, A.K.,	J.Text.Inst. 37, P.371, 1940.
56	GOODING, A.C. AND TURL, L.H.,	Ibid, 31, T.69, 1940.
57	HARBURTON, F.L.,	Ibid, 38, T.65, 1947.
58	KIRGENSONS, B.,	J.Polymer.sci., 1, 475, 1946.

59 SHARKWEATHER, H.W. JR., GEORGE, M., HANSEN, J.E., RODEE, T.M., AND BROOKS, R.E., ibid, 21, 189, 1956.

60 VALENTINE, L., Annals. Textiles, 12, 207, 1955.

61 URQUHART, A.R., AND WILLIAMS, A.M., J.Text.Inst. 15, T.559, 1924.

62 URQUHART, A.R., AND ECKERSALL, N., ibid, 21, T.499, 1930

63 SPEAKMAN, J.B., AND COOPER, C.A., ibid, 27, T.191, 1936.

64 SPEAKMAN, J.B., J.Soc.chem.Ind., 49, T.209, 1930.

65 HUTTON, E.A., AND GARTSIDE, J., J.Text.Inst, 40, T.170, 1949.

66 PEIRCE, F.T., ibid, 20, T.133, 1929.

67 HERMANS, P.H., Physics and Chemistry of Cellulose Fibres, Elsevier, Amsterdam, 1949.

68 BARNES, R.B., BURTON, C.J. AND SCOTT, R.G., J.App.Phys. 16, 750, 1945.

69 KERN, S.F., J.Polymer.sci, 1, 259, 1946.

70 MARK, H., J.Phys.chem, 44, 764, 1940.

71 HERMANS, P.H., HEIKENS, D., AND WEIDINGER, A., J.Polymer.sci., 35, 159, 1959.

72 HERMANS, P.H., AND WEIDINGER, A., Makromol.chem. 39, 67, 1960.

73 FLORY, P.J., SPURR, O.K., AND CARPENTER, D.K., J.Polymer.sci., 27, 231, 1958.

74 COOKE, D.M., AND WARWICKER, J.O., Chim. and. Industr. 804, 1961.

75 ZIMMERMANN, J., AND MARTIN, F., Chem.Zentr. 1, 856, 1937.

76 WILLIAMS, J.W., AND DANIELS, F., J.Amer.Chem.Soc., 46, 903, 1924.

77 WALDEN, P., AND WERNER, O., Z.Physik.chem., 111, 465, 1924.

78 JONES, J.M., J.Sci.Inst., 38, 367, 1961.

79 MEREDITH, R., AND PYE, I.A., Text.Institute and Industry., 2, 154, 1964.

80 MORTON, W.E., AND HEARLE, J.W.S., "Physical properties of Textile fibres" Butterworths, London, 1962.

81 MULLINS, M.F., "The Technology of Polyester Fibres". New York, 1965.

82 HAHN, F.C., MACHU, M.L., AND FLETCHER, D.A., Ind.Eng.Chem., 37, 526, 1945.

83 NATTA, G., AND CORRADINE, P., J.Polymer.sci., 39, 29, 1959.

84 SLINCHER, W.P., AND MANSLA, F.R., J.App.Phys., 29., 1459, 1958.

85 HEMSTEAD, W., J.Text.Inst., 52, P.148, 1961.

86 HUNTER, E., AND OAKES, W.G., Trans.Farad.Soc., 41, 49, 1945.

87 MIGA, P.V.O., Physical Properties of Polymers, No.5, New York, 1959.

88 DADAMI, D.V., CHAPPEL, F.P., CULPIN, M.F., JONES, D.M., AND TRAINER, T.G., Rheol.Acta. 1, 639, 1961.

89 O'BRIEN, F.E.M., J.Sci.Inst., 25, 73, 1948.

90 LAROSE, P., Text.Res.J. 34, 80, 1964.

91 BOYER, R.F., AND SPENCER, R.S., J.App.Phys., 15, 398, 1941.

92 PASSAGLIA, E., AND KOPPEHELE, H.P., J.App.Polymer.Sci., 1, 29, 1959.

93 UEBREITER, K., Z.Physik.Chem., 348, 197, 1941.

94 DAVIS, M.L., J.App.Polymer.Sci., 1, 121, 1959.

95 SHIMIZAWA, T., GUPTA, V.D., TURNER, R., DILLON, J.H., AND TOBOLSKY, A.V., Text.Res.J., 32, 810, 1962.

96 AKUTA, N., TOYAMI, H., AND YOKOTA, D., J.Soc. Text.Cellulose.Ind. (Japan) 10, 310, 1954.

97 STEELE, R., AND SCHWALL, R.P., Text.Res.J., 29, 228, 1959.

98 MEHTA, P.M., Unpublished, Ph.D. Thesis University of Glasgow, 1964.